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<b>(54) Title:</b> LOW DENSITY MATERIALS HAVING HIGH SURFACE AREAS AND ARTICLES FORMED THEREFROM FOR USE IN THE RECOVERY OF METALS			
<b>(57) Abstract</b> <p>A porous body derived from a polymeric material, e.g. a gel-forming polymeric material, said body having an open-celled 3-dimensional lattice structure, a density of less than about 1.0 g/cc (cubic centimeter) and a surface area equal to or greater than about 85 m<sup>2</sup>/g. In accordance with another embodiment a method for the removal of a desired material, such as metal(s), from a fluid stream employs one or more porous bodies of this invention as the contacting material which removes the desired material from the fluid stream.</p>			

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**LOW DENSITY MATERIALS HAVING HIGH SURFACE  
AREAS AND ARTICLES FORMED THEREFROM  
FOR USE IN THE RECOVERY OF METALS**

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**1. Field of the Invention**

This invention relates to novel porous bodies which possess a relatively low density (generally less than about 1.0 g/cc), and a relatively high surface area (at least about 85 m<sup>2</sup>/g) as well as one or more other beneficial properties such as pore volume and strength characteristics, all of which are favorable for many industrial applications, such as insulating materials, fibers, absorbents, adsorbents, ion-exchange resins, membranes and support materials for a wide variety of uses. The porous bodies have an open-celled 3-dimensional lattice structure. The novel bodies can be flexible, semi-rigid or rigid. The invention also relates to articles formed from the porous bodies, modified forms of the porous bodies, processes for preparing the porous bodies and articles formed therefrom. The highly porous low density articles can easily be modified chemically for a desired application, for example, filtration and recovery of organics or inorganics, specifically metals, as well as supports for immobilizing enzymes. The porous bodies can be prepared from polymeric materials. In many instances, the porous bodies of this invention are formed from hydrogels.

30   **2. Prior Art**

Numerous attempts have been made to make low density solid materials. For instance, low density materials have been prepared from aerogels. Aerogels have been made from iron and tin oxides, aluminas, tungsten, biopolymers and, more commonly, silicas. The first aerogels were produced in the early 1930's (Kistler, Stanford University) by exchanging the water in sodium silicate with an alcohol, and then removing the alcohol under high temperature and pressure (81 bars, 240°C).

Using the same basic original technique, it was possible to produce materials with densities in the range of 0.03 to 0.3 g/cc. For further detailed information, refer to Kevin J. Anderson, "From 5 Aquagels to Aerogels", Materials Research Society Bulletin, March 1991. During 1990, Hrubesh of The Lawrence Livermore National Laboratory modified the technique by using a condensed silica form, base catalyst and supercritical fluid extraction to achieve 10 porous solids of silica aerogels having ultra low density of about 0.005 g/cc (See Robert Pool Science, 247 (1990), at 807). One disadvantage of such materials is that at these densities the porous solids are expected to have limited strength properties. Secondly, 15 the aerogels can be somewhat difficult to modify (chemically) for various commercial applications. Another disadvantage of the Hrubesh method is the use of the expensive supercritical fluid extraction procedure. Although alumina supports having densities 20 of 0.3 g/cc or less can be prepared with special processes, the porous material obtained possesses minimal cohesive integrity and, thus, it tends to crumble under pressure. In fact, under microscopic examination, such alumina supports appear to be 25 conglomerates or aggregates of particles held together by short-range electrostatic or hydrogen bonding forces.

Others have attempted to crosslink polymeric gel materials, such as chitosan. Japanese Patent 30 Publication No. 61-133143 published June 20, 1986, by S. Tokura and K. Seo disclose a heavy metal adsorbing agent which is made by dissolving low molecular weight chitosan in acidic water solution and coagulating said solution in a basic solution to obtain porous chitosan 35 and then crosslinking this using an organic

diisocyanate compound. The chitosan product is noted as having a surface area of 84.6 m<sup>2</sup>/g.

SUMMARY OF INVENTION

5 This invention relates to a porous body derived from a polymeric material, said body having an open-celled 3-dimensional lattice structure, a density of less than about 1.0 g/cc (cubic centimeter) and a surface area equal to or greater than about 85 m<sup>2</sup>/g.

10 This invention also relates to an article formed totally or in part from a porous body of this invention.

15 This invention also relates to composition comprising one or more porous bodies of the invention and at least one material other than said one or more porous bodies.

20 Further embodiments relate to a polymer composition comprising one or more porous bodies of this invention and at least one polymer material which is not a porous body of this invention as well as articles formed from such compositions.

25 Another embodiment of the invention relates to an apparatus for removal of a desired material from a fluid stream comprising one or more porous bodies of this invention and a vessel which comprises an inlet and outlet means for inflow and outflow of said fluid stream.

30 An additional embodiment relates to a method for the removal of a desired material from a fluid stream comprising the desired material comprising contacting a fluid stream with one or more porous bodies of this invention.

35 One of the novel methods of this invention relates to a method for the removal of one or more metals from a fluid stream containing the metal or metals, which

process comprises contacting said fluid stream containing one or more metals with one or more porous bodies of this invention. The methods for removal of metals provides an efficient technique for the removal 5 of heavy metals, including precious metals and radioactive metals, such as uranium.

It is noted that the various materials and methods of this invention described herein can be used to remove inorganic and organic materials from fluid 10 streams.

1. **Gel** - a colloid in which a dispersed phase is formed in a continuous phase, wherein said 15 continuous phase is formed from a liquid and the colloid maintains a desired shape.
2. **Pre-gel** - colloid and solution having a dispersed phase in a continuous phase, said continuous phase formed from a liquid. A pre-gel is free-flowing and does not maintain a desired shape on its own. 20
- 25 3. **Gel-forming material** any material capable of forming the dispersed phase of a gel or pre-gel.
- 30 4. **Gelling Solvent** any material in the presence of which a gel-forming material can form a pre-gel or gel.
- 35 5. **Hydrogel** any gel-forming material which is capable of forming a pre-gel or gel in water.

## 6. Body

a form of a 3-dimensional material having a size at least greater than a particle size of 0.5 cm in any dimension.

5

DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing which depicts a porous body of this invention and its open-celled 3-dimensional lattice structure.

Figure 2 is an electron micrograph of a porous body formed from sodium alginate.

Figure 3 is schematic drawing showing an apparatus having therein a plurality of the porous bodies of this invention.

Figure 4 graphs the results obtained in Example 4.

Figure 5 is a graph of the results obtained in Example 8.

Figure 6 is a graph of the results obtained in Example 9.

Figure 7 is a graph of the results obtained in Example 10.

Figure 8 is a graph of the results obtained in Example 11.

Figure 9 is a graph of the results of Example 12.

Figures 10 is a graph of the results of Example 13.

Figure 1 depicts a section of the open-celled 3-dimensional lattice of a porous body of this invention.

The porous body 10 has pores 11 and 12 which form a continuous network of pores.

In Figure 3, an apparatus 20, is shown having an inlet means 21 and an outlet means 24. The apparatus 20 contains a plurality of the porous bodies (23) of this invention.

DETAIL DESCRIPTION OF THE INVENTION

As noted, one embodiment of the invention relates to a porous body derived from a polymeric material, 5 said body having a 3-dimensional open-celled lattice structure formed from a crosslinked polymer and a density of less than about 1.0 g/cc and a surface area of at least about 85 m<sup>2</sup>/g as well as articles formed totally or in part therefrom. The term lattice as used 10 herein refers to an open framework of crosslinked polymer. Open-celled emphasizes the nature of the lattice structure itself and that the inner walls of the lattice structure form a network of open cells throughout the body (See Figure 1). Figure 1 depicts a 15 section of a porous body 10 of this invention, the lattice structure formed by the crosslinked polymer and pores 11 and 12 that form the network of open-cells throughout the porous body 10. The pores may vary in diameter and size. The porous body possesses one or 20 more beneficial properties. These beneficial properties include the relatively low density and high surface area of the body as well as relatively high pore volume and relatively small pore diameter. In addition, the porous body has excellent strength 25 characteristics as exemplified by compression yield. The numerous beneficial properties of the body provide a material with virtually unlimited uses, such as support materials, fillers, absorbents, adsorbents, filters, fibers, membranes and many other applications. 30 The density as well as other properties of the body can be adjusted to specifications for particular applications of the article.

The novel porous body of this invention can take on virtually any desired form. For example, it can be 35 formed as a bead, pellet, cube, box-like rectangular

shape, sphere, cylindrical body, such as a tube or fiber, or flat bodies such as sheets, membranes and coatings.

Generally, the body has a low density of less than  
5 about 1.0 g/cc. The density of the porous body is selected for the desired application as appropriate. In preferred embodiments, the density of the body is less than about 0.8 g/cc. In more preferred  
10 embodiments, the density is less than or equal to about 0.6 g/cc. In further preferred embodiments, the density is less than or equal to about 0.5 g/cc. In particularly preferred embodiments, the density is equal to or less than about 0.3 g/cc. In more particularly preferred embodiments, the density is  
15 equal to or less than 0.2 g/cc. In further preferred embodiments, the density is equal to or less than 0.15 g/cc. In alternative embodiments, the density can be as low as less than about 0.1 g/cc or even less than about 0.05 g/cc. However, preferably, the body has a minimum  
20 density which is at least sufficient to maintain the 3-dimensional lattice structure of the body. In many preferred embodiments of the invention, the body has a density of at least about 0.01 g/cc, and, preferably of minimum density of at least 0.02 g/cc.  
25 As noted, the porous bodies are lightweight, i.e. low density, but the novel materials of this invention also have excellent surface area characteristics. The beneficial surface area characteristics of the body can play a substantial factor in the utility of porous  
30 bodies and articles formed therefrom. For example, with a first material having more surface exposed than other materials, the available surface area for attachment of active agents, filtration or adsorption of materials is increased in the first material. An increase in  
35 surface area per gram of a material often minimizes the

amount of material needed to perform a desired function. The ability of given amount of material to perform as an adsorbent can be viewed as a function of the amount of adsorption per gram of material. The more 5 surface area per gram, the better the material will function as an adsorbent.

Generally, the porous open-celled 3-dimensional lattice body has a surface area of at least about 85 m<sup>2</sup>/g. Preferably, said surface area is at least about 10 150 m<sup>2</sup>/g. In further preferred embodiments, this surface area is at least about 200 m<sup>2</sup>/g. In particularly preferred embodiments, the surface area is at least about 250 m<sup>2</sup>/g. In more particularly preferred embodiments, the surface area is at least about 300 15 m<sup>2</sup>/g, with the surface area of choice being at least about 350 m<sup>2</sup>/g.

The open-celled nature of the porous bodies of this invention can be further characterized in part by pore volume and pore diameter.

20 The following pore volumes are noted to be of interest for practice of this invention. Preferably, the pore volume is at least about 1 cc/g. More preferably, the pore volume is at least about 1.5 cc/g. In further preferred embodiments, the pore volume is at 25 least about 2.0 cc/g. In particularly preferred embodiments, the pore volume is at least about 2.5 cc/g. In more particularly preferred embodiments, the pore volume is at least about 3.0 cc/g. In alternative embodiments, the pore volume is at least about 3.5 cc/g. In the most preferred embodiments, the pore 30 volume is at least about 4.0 cc/g.

The pore diameter can vary substantially to achieve a given pore volume. Generally, the open-celled lattice structure of the body has an average 35 pore diameter of at least about 50 Angstroms (Å). In

preferred embodiments, the average pore diameter is at least about 100 Å. In more preferred embodiments, the body has an average pore diameter of at least about 200 Å. In particularly preferred embodiments, the average 5 pore diameter is at least about 250 Å. In more particularly preferred embodiments, the average pore diameter is at least about 300 Å. In further preferred embodiments, the average pore diameter is at least about 350 Å. In alternatively preferred embodiments, 10 the average pore diameter ranges from about 50°Å to about 500 Å.

In alternative embodiments of the invention, one can vary the average pore diameter to accommodate (or discriminate against) many different materials or 15 specific applications. For example, in preferred embodiments of the invention one can use articles having an average pore diameter of about 150 to 400Å to entrap or immobilize a specific molecule such as an enzyme within the pores of a shaped body. For other 20 applications, such as forming insulation materials from materials of this invention, a relatively small pore (10 to 150 Å) may be desired. For applications in which rapid diffusion is important, one can use a relatively large pore diameter, as needed. Control of 25 the pore diameter also permits one to selectively discriminate molecules which are not to enter the pores of the body.

It is important to note that as the density of the material is decreased, the average pore diameter is 30 observed to increase; thus, there will also be a range of pore diameters associated with a given density. However, the pore diameter can be varied by employing a "ghost" mold or imprint technique. The "ghost mold" or 35 imprint technique involves adding to the gel a material (prior to, during, or after gelation) which can be

removed from the gelled material at another period during processing. The ghost material creates a void of space when removed. It can be removed by conventional techniques known in the art, such as 5 dissolving or chemically etching the "ghost" material from the porous body derived from the gel-forming material.

Surprisingly, in spite of the relatively low density of the bodies and articles formed therefrom, 10 they also possess beneficial strength characteristics for a desired utility (e.g. support). The open-celled 3-dimensional lattice structure is believed to provide much of the strength. The porous body, e.g. a cube, pellet or bead, has a compressive strength such that, 15 when subjected to pressure the body does not fall apart or collapse. Basically, the porous bodies of this invention have a relatively low amount of yield. A yield measurement for compression corresponds to a stress-strain curve which is measured for a given 20 amount of pressure applied to a material of known dimensions. This curve reflects the amount of compression resulting from the applied pressure. See Sibilia's A Guide to Materials Characterization and Chemical Analysis VCM Publishers 1988, 273-275.

25 Preferably, the compression strength is equal to or less than 50% yield at 300 psi, pounds per square inch. In further preferred embodiments, the compression strength is equal to or less than 40% yield at 300 psi. In particularly preferred embodiments, the compression 30 strength is equal to or less than 25% yield at 300 psi. In more particularly, preferred embodiments, the compression strength is equal to or less than about 10% yield at 300 psi. In alternative embodiments, the compression strength is equal to or less than about 10% 35 yield at 1000 psi.

In the embodiments of this invention, the porous bodies have densities of less than about 1.0 g/cc. It should be noted that the density of the body is indirectly proportional to the strength characteristics 5 of that body. At higher densities, the yield measurement (at a given applied pressure for an article) will be less than a yield measurement for an article having a lower density.

As discussed above, the porous bodies of this 10 invention are derived from a polymeric material. The polymeric nature of the material is believed to provide the 3-dimensional lattice structure of the porous body. The polymer chains form the basic framework of the porous body and these polymer chains are crosslinked to 15 an extent sufficient to maintain the polymer chains in the desired configuration. The polymeric materials have functional groups along the polymer which can form covalent bonds with corresponding functional reactive groups of a crosslinking agent. The number of 20 functional groups along the polymer is sufficient to provide a crosslinked density throughout the 3-dimensional lattice such that the crosslinked material forms an open-celled 3-dimensional lattice structure which remains intact after removal of solvent from the 25 crosslinked gel. Preferably, at least 2% of the functional groups along the polymer are crosslinked.

Preferably, the porous body is formed from a natural or synthetic gel-forming polymer. Natural polymers are polymers that are present in nature and 30 include polymers which are isolated from living organisms. Synthetic as used herein refers to non-naturally occurring polymers produced by chemical methods, chemically modified natural polymers as well as materials produced by recombinant techniques. In 35 further preferred embodiments of the invention, the

porous body is formed from a hydrogel polymer, which may also be either natural or synthetic; however, natural hydrogel materials are preferred. In more preferred embodiments the hydrogel material is a 5 protein, including glycoproteins, or a polysaccharide.

In additionally preferred embodiments, the polymer is a gel-forming material, such as a polysaccharide or protein. ~~Illustrative of polysaccharides and proteins useful in the practice of the invention are chitosan, carageenan, pectin, gelatin, collagen, locust bean gum, guar gum and agar.~~ In further preferred 10 embodiments, the gel-forming material is selected from naturally-occurring extracts. ~~Illustrative of such materials are gelatin, chitosan and alginates, such as group I metal alginates, specifically sodium alginate,~~ which is obtained from seaweed. Other useful gel-forming materials are conventional polymer gels used as 15 thickeners, especially those which are used as additives in the food industry.

Synthetic polymers which may be used include 20 polyacrylamides, polysulfones, polyols, such as polyvinyl alcohols and polyvinyl acetates and acrylate polymers, as well as crosslinkable polymers copolymers, such as polymethacrylates,

polyvinylpyrrolidones and derivatives thereof.

Preferred embodiments are directed to polymers formed from monomers which may be polymerized and crosslinked to produce hydrogels, such as the following monomers:

the family of methacrylates including methyl 25 methacrylate, methacrylic acid, hydroxyethyl methacrylate, hydroxyethoxyethyl methacrylate, methoxyethyl methacrylate, methoxyethoxyethyl methacrylate, methoxydiethoxyethyl methacrylate, aminoethyl 30 methacrylate propylene, glycol methacrylates and 35

derivatives thereof. Some crosslinking agents which may be used for these monomers include ethylene glycol dimethacrylate, other dimethacryl monomers, divinylbenzene, etc. Other monomers which may be useful to form polymer hydrogels include vinyl alcohol, 5 vinyl acetate, N-vinyl-2-pyrrolidone, sodium vinyl sulfonate, sodium styrene sulfonate, pyridine, acrylamide derivatives, acrylic acid derivatives, methylene-bis-acrylamide, crotonic acid, 2,4-pentadiene-1-ol, etc. These monomers may be polymerized and crosslinked to form polymers, 10 copolymers, block copolymers and graft copolymers by conventional methods as known in the art. See Peppas, N.A., Hydrogels in Medicine and Pharmacy, CRC Press, 15 Inc., Boca Raton, 1986.

In particularly preferred embodiments, the gel-forming material is a natural or synthetic form of gelatin, chitosan, alginates, agar or derivatives thereof. In more particularly preferred embodiments, 20 the gel-forming material is derived from gelatin, chitosan, alginate or derivatives thereof such as metal salts. In the case of alginate, the sodium salt is the most preferred.

The porous bodies of this invention are preferably prepared by a novel process which employs a gel-forming polymer as a precursor material. Because a gel composition is predominantly a liquid, it has been difficult to remove the liquid component without causing the dispersed phase of gel-forming material to 25 simply collapse, creating a material having a density which is greater than 1 g/cc. Generally, any potential structure, formed by the gel-forming material within the gel is substantially destroyed upon removal 30 of the gelling solvent. The present invention provides 35 a process which enables one to remove the gelling

solvent from a gel and also maintain the dispersed phase of the gel in order to form a porous body having an open-cell 3-dimensional lattice structure. Since the gel is constituted mainly of the gelling solvent, once 5 the solvent is removed, the resulting body has a relatively low density (i.e. less than 1.0 g/cc).

One novel process for preparing the porous bodies of this invention comprises:

- 10 1. forming a gel of a desired configuration;
2. (i) preparing the gel for crosslinking by replacing the initial gelling solvent directly or indirectly with a crosslinking solvent which does not react with a
- 15 crosslinking agent by employing a concentration gradient of solvent to replace the gelling solvent;
- (ii) adding an effective amount of crosslinking agent; and
- 20 3. separating the crosslinked body from the crosslinking solvent.

In the preferred embodiments, the process for preparing the articles of this invention comprises:

1. forming a gel of a desired configuration;
- 25 2. (i) preparing the gel for crosslinking by replacing the initial gelling solvent with one or more intermediate solvents by employing a concentration gradient, and then replacing the intermediate solvent with a crosslinking solvent;
- (ii) adding an effective amount of crosslinking agent; and
- 30 3. separating the crosslinked body from the crosslinking solvent.

35 In an alternative embodiment, the process for

preparing the articles of this invention comprises:

- (1) crosslinking the gel-forming material of the gel by adding thereto an effective amount of a crosslinking agent, which is not reactive with the gelling solvent of the gel.
- 5 (2) removing the solvent from the crosslinked gel-forming material while maintaining the open-celled 3-dimensional lattice structure of the crosslinked gel-forming material to form a porous body which contains no or substantially no solvent.

The first step requires a gel as a starting material. Conventional methods of forming pre-gels or gels can be used. Some materials can be added to a 15 gelling agent, and a free-flowing pre-gel naturally occurs. Many materials may require the addition of a pre-gel additive, which causes the formation of a pre-gel from the gel-forming material in the gelling solvent. Some pre-gels may require the use of a 20 gelling agent to form a gel from the pre-gel state other gel-forming materials form a gel directly from a gel-forming material and gelling solvents. Other gel-forming materials form a gel directly from a gel-forming material and gelling solvents. In some 25 instances, the gel-forming material forms a pre-gel or gel upon a gelling treatment step without a gelling agent. For example, agar will form a gel upon heating to at least about 80°C and cooling until gelation occurs. The methods of forming the pre-gels and gels 30 are well-known in the art.

The starting amount of gel-forming material directly affects the density of the porous body. With an increase in the concentration of gel-forming material, the density of the porous body increases. An 35 effective amount of gel-forming material is used. An

"effective" amount is the concentration of gel-forming material in a gelling solvent which is sufficient to form a gel in a desired amount of gelling solvent. The effective amount of gel-forming material will vary with  
5 the selected density of the porous body.

The choice of pre-gel additive used varies with the choice of gel-forming material. An effective amount of pre-gel additive is that amount which is sufficient to cause a given amount of gel-forming  
10 material to form a pre-gel in a gelling solvent. The effective amount will vary with the amount of gel-forming materials used according by the known methods of preparation.

Preferably, once the pre-gel is formed, the pre-gel is centrifuged to remove air bubbles which may form during mixing and forming the pre-gel. This step aids in obtaining a substantially homogeneous porous body. A non-homogeneous porous body may contain an abundance of voids which may decrease physical properties such as  
20 strength.

The first step of the process comprises forming a gel of a desired shape. Shaping may be carried out by any conventional methods known in the art. A pre-gel can be placed in a mold of any desired shape and then  
25 treated by conventional methods to form a gel. For example, a layer of the pre-gel can be placed on a flat surface to form a sheet. The pre-gel can be expressed through an aperture to form a filament fiber or tube. The pre-gel is treated as it is expressed through the  
30 aperture to form the gel. A layer of pre-gel can also be placed on a cylinder to form a tubular shape. Thus, shapes can vary substantially to form any desired configuration (tubes, cubes, rectangular shapes, sphere, such as beads, pellets, sheets, which may be in  
35 the form of membrane).

Preferably, once a pre-gel is placed in a mold or shaped as desired, it is preferably exposed to a gelling agent to set or coagulate the gel in order to maintain the desired shape. A gelling agent interacts 5 with strands of the gel-forming material of the pre-gel to orient the strands in an ordered state.

The pre-gels can be exposed to a solution of an effective amount of gelling agent. As used herein, an effective amount of gelling agent is that amount of 10 gelling agent which is sufficient to set or coagulate the pre-gel such that the desired shape is maintained. As a gel the shape is no longer in a free-flowing state; it is self-standing, yet it is not in solid state. Appropriate amounts of gelling agent will vary 15 in amount with the amount of each gel-forming material; however, each gel can be prepared by conventional techniques known in the art. For example, for sodium alginate, preferably, at least about .05 molar concentration of gelling agent is used. More 20 preferably, a concentration of at least about 0.1 M of gelling agent is employed. In further preferred embodiments, the concentration of gelling agent is at least about 0.2M.

The setting or coagulation of the pre-gel step 25 takes place over time. The amount of time required for this gelling to take place is dependent upon the diffusion of the gelling agent throughout the gel. The gel's viscosity (resulting from the amount of gel-forming material used in forming the gel) generally 30 dictates the length of time needed for the movement of the gelling agent throughout the gel. The higher the concentration of gel-forming material in the gel, the longer the diffusion time will be. Gelling time may also involve a molecular rearrangement of the gel-forming material. To some extent the re-arrangement 35

18 will occur simultaneously with the diffusion of the setting agent through the gel. This re-arrangement may also continue to occur after diffusion of the gelling agent through the gel. It is believed that without diffusion of the gelling agent throughout the gel, shrinkage or collapse of the gel can occur during the downstream process steps of forming the porous body. With the onset of shrinkage, density may increase (as surface area decreases) to a point above a desired level.

10 The choice of gelling agent will vary with the type of gel-forming material used therein. The gelling agent can be any agent which is reactive with the gel-forming material to set or coagulate the pre-gel. Often the gelling agent will be inorganic or organic acid or base, e.g. for chitosan and gums. On the other hand, in the case of alginate, an inorganic or organic cationic material is used to ionically bond the carboxylic acid moieties of the polymer strands of the alginate. Preferably, the gelling agent for alginate is a dicationic or polycationic inorganic or organic material which is able to ionically bond the carboxylic acid moieties of two adjacent polymer strands.

15 Sodium alginate can be gelled using organic acids such as sodium alginate, can vary widely. Illustrative such acids are acetic acid, propanoic acid, butanoic acid, benzoic acid, oxalic acid, malonic acid, succinic acid adipic acid, glutaric acid, maleic acid, phthalic acid and derivatives thereof. Preferably, a dicationic metal or a dicarboxylic acid is employed in order to link two strands of gel-forming material together. Cationic ions include ionic forms of and of the following: Al, Ba, Ca, Mg, Sr, Cr, Cu, Fe, Mn, and

Zn. Most of the transition metals in the cationic form of  $X^{2+}$  or more can also be employed. Preferably the cationic metal is a cationic form of Ca, Ba or Cu.

The gelling agent or process used to gel  
5 the pre-gel depends on the gel-forming material used. For example, although chitosan is initially forms a pre-gel in acid solution, the chitosan is coagulated or set in a solution containing base to form a gel. Preferably, for chitosan, the solution of gelling agent  
10 is a dilute solution, which is at least about 2% base. In further preferred embodiments, the base solution has a concentration of at least 5% base. In particular preferred embodiments, the base is solution at least about 10% base. Inorganic and organic bases may be  
15 employed dependent on the gel-forming materials selected. One inorganic base typically used is sodium hydroxide.

An alternative to using a gelling agent is a gelling treatment process. Illustrative of such a  
20 process is a rapid cooling treatment process. Such a process may be used in addition to a separate gelling technique. The rapid cooling technique, involves forming a pre-gel or gel and dropping the pre-gel or gel into a solvent bath which has been cooled to a  
25 temperature at least above the freezing point of the gelling solvent used in forming the gel. For hydrogel materials, generally, water alone is not used as a gelling solvent for the rapid cooling technique since water will freeze and will not diffuse out. Generally,  
30 a water/organic solvent mixture is used for applying the rapid cooling technique to hydrogels. In the case of alginate, a water/ethylene glycol (having at least about 25% ethylene glycol or organic solvent) can be used as the gelling solvent. The pre-gel or gel is  
35 then placed in a cooled bath of acetone. The acetone

replaces the water/ethylene glycol solvent.

In the second step of the process of this invention, the gel is prepared for crosslinking by replacing the initial gelling solvent with a crosslinking solvent. The gelling solvent can be replaced directly with a crosslinking solvent or indirectly with one or more intermediate solvents and then with a crosslinking solvent. The crosslinking solvent should be miscible with the gelling solvent or intermediate solvent if an intermediate solvent is employed. The crosslinking solvent should also be non-reactive with gel-forming material and crosslinking agent. The surface tension of the crosslinking solvent can be less than, greater than or equal to the surface tension of the gelling solvent. Preferably, the crosslinking solvent has a surface tension substantially equal to the gelling solvent. This would obviate the necessity for solvent exchanges over a concentration gradient as discussed infra. In alternative embodiments, the crosslinking solvent has a surface tension which is less than the gelling solvent. In such embodiments, the crosslinking solvent may have a surface tension which is less than or greater than that of the intermediate solvent. In more preferred embodiments, the crosslinking solvent has a surface tension which is less than about 75 dynes/cm. In further preferred embodiments, the crosslinking agent has a surface tension equal to or less than about 50 dynes/cm. In particularly preferred embodiments, the crosslinking solvent has a surface tension equal to or less than 40 dynes/cm. In more particularly preferred embodiments, the crosslinking solvent has a surface tension equal to or less than about 30 dynes/cm.

Illustrative of solvents useful in the practice of the invention are chloroform, dimethyl sulfoxide,

pyridine and xylene. In many of the preferred  
embodiments, the crosslinking solvent is an aprotic  
organic solvent.

In alternative embodiments in which a crosslinking  
solvent has a surface tension greater than that of the  
gelling solvent, a concentration gradient as described  
supra is employed to replace the gelling solvent with  
the crosslinking solvent.

In many cases, a crosslinking agent may be  
reactive with a gelling solvent therein, the gelling  
solvent should be substantially, if not completely,  
removed from the gel prior to crosslinking. Reaction  
of the gelling solvent and crosslinking agent can  
diminish the crosslinking of the gel-forming material  
and/or prevent removal of the gelling agent.

crosslinked gel. For example, the water in a hydrogel  
will react with a crosslinking agent such as, tolylene  
diisocyanate (TDI). The replacement of the gelling  
solvent with the crosslinking solvent is generally  
referred to herein as a solvent exchange step. The  
actual exchange to the crosslinking solvent is generally  
initial gelling solvent may comprise one or more  
exchanges of the gelling solvent with an intermediate  
solvent or solvents prior to replacing the intermediate  
solvent with the crosslinking solvent.

Preferably, the solvent exchange process comprises  
replacing an initial gelling solvent, e.g. water, with  
an intermediate solvent of low surface tension, e.g.  
acetone. The intermediate solvent is selected such  
that is miscible with both the gelling solvent and with  
the subsequent intermediate solvent or crosslinking  
solvent. Preferably, the intermediate solvent has a  
surface tension which is lower than that of the gelling  
solvent. In more preferred embodiments the  
intermediate solvent has a surface tension of less than

75 dynes/cm. In further preferred embodiments, the intermediate solvent has a surface tension equal to or less than about 50 dynes/cm. In particularly preferred embodiments, the intermediate solvent has a surface 5 equal to or less than about 40 dynes/cm. In more particularly preferred embodiments, the intermediate solvent has a surface which is equal to or less than about 30 dynes/cm.

It is noted that if a crosslinking solvent has a 10 surface tension greater than that of the gelling solvent, preferably, if an intermediate solvent is used the intermediate solvent has a surface tension which is less than the surface tension of the crosslinking solvent and greater than the surface tension of the 15 gelling solvent.

If more than one intermediate solvent is used, then the intermediate solvent need only be miscible with the solvent used prior and the solvent used subsequently. For example, in the case of hydrogel, 20 water can first be exchanged with acetone, which is miscible both with water and with a subsequent crosslinking solvent such as toluene. Acetone is one of the preferred intermediate solvents because of several considerations. Acetone is readily available and is 25 relatively innocuous. It is also soluble in water and toluene. Other solvents which can be used include alcohols, such as methanol, ethanol, propanol and butanol, acetates, e.g. methyl and ethyl acetate, DMSO, DMF etc. Toluene is often selected as a solvent 30 for crosslinking because it is an aprotic solvent with minimal affinity for water. It is also relatively non-reactive with the crosslinking reagents used herein.

In order to maintain the structure of the gel, without causing the shrinkage or collapsing of the gel 35 upon removal of the gelling solvent, care must be taken

when replacing the gelling solvent with the intermediate solvent. There may also be a need for a number of gradual solvent exchanges using the same intermediate solvent at various increasing concentrations, i.e. concentrations of intermediate solvent in solvent used prior or gelling solvent. The solvent exchange of the same solvent at gradual intervals is herein referred to a solvent exchange over a concentration gradient. The concentration gradient can be used to decrease stepwise the surface tension of the liquid component within the gel. Generally, an effective concentration gradient is an interval of changes in concentration of intermediate solvent which does not cause a collapse of the gel structure to the extent that the porous body cannot be formed or has a density greater than 1g/cc. If the gel collapses, a product of low density is not achievable. The set gel is exposed to one or more intermediate solvents in a graduated fashion employing an effective concentration gradient in order to avoid substantial shrinkage of the gel. More preferably, an initial concentration of intermediate solvent should range from about 5 to about 25% and the solvent exchanges over the concentration gradient can then take place with increases in concentration of 10% or more. The intermediate solvents are usually a mixture of the intermediate solvent and the gelling solvent until 100% intermediate solvent is exchanged.

In further preferred embodiments, the concentration gradient comprises employing an initial concentration ranging from about 10 to 25% and then the concentration of the intermediate solvent is stepped up at increases of from about 15 to about 25%. An incremental increase of 20-25% is particularly preferred to minimize the number of solvent exchanges.

Once a substantially complete exchange of intermediate solvent for the initial gelling solvent is conducted, the intermediate solvent can generally be exposed directly to 100% of the crosslinking solvent. Although 5 it is theorized that for most gel-forming materials no gradient is required for the exchange from the intermediate solvent to the crosslinking solvent, there may be a situation where a concentration gradient is used for the exchange of an intermediate solvent and a 10 crosslinking solvent. Preferably, once the exchange to the crosslinking solvent is performed, a wash step is performed using the crosslinking solvent to remove any traces of intermediate solvent or initial gelling solvent which might interfere with the crosslinking 15 reaction.

For each solvent exchange step, one should allow sufficient time for the replacement solvent to reach equilibrium. Equilibrium is the point at which the concentration of the replacement solvent inside the gel 20 is in equilibrium with the concentration of the replacement solvent at the outer surface of the gel. Preferably, at least one solvent exchange is performed. In many of the preferred embodiments at least two solvent exchanges are performed. The number of solvent 25 exchanges may vary thereafter from 2 to 10. For any exchange protocol, one attempts to minimize the number of steps used and the amount organic waste generated in each batch of exchanges. Generally, intermediate waste is reused, redistilled or separated to recover the 30 solvents.

In alternative embodiments, additional techniques may be performed to prepare the gel for crosslinking. These techniques may be performed in addition to or instead of the solvent exchange processes. Although, 35 these processes may be used instead of the solvent

exchange, it may be preferable to perform at least one solvent exchange during or prior to such techniques. Illustrative of such alternate techniques are freeze-drying and supercritical fluid extraction. Freeze-

5 drying is advantageous since a solvent exchange procedure should not be necessary. On the other hand, a supercritical fluid extraction can also be beneficial since water can be exchanged by this method with or without the need for intermediate solvent exchanges.

10 Freeze drying is a well-known procedure which is frequently used in the food industry to dry a material. A sample to be freeze-dried is first cooled to a temperature below the freezing temperature of the solvent in which the gel-forming material is

15 dissolved and then subjected to vacuum drying by methods known in the art. This causes the solid crystals to sublime.

Another technique which can be used in addition to or instead of the solvent exchange method is a super-  
20 critical fluid extraction process. Basically, this process involves extractions of the gelling solvent or intermediate solvent at high pressure using supercritical CO<sub>2</sub> in the liquid phase. Supercritical CO<sub>2</sub> is non-polar and can replace the solvent present in  
25 the gel. When the pressure is released, the CO<sub>2</sub> is evacuated from the porous material. This technique can be used in a similar way to that which is currently used for the preparation of inorganic aerogels, a method known in the literature. In using the freeze-  
30 drying method or supercritical extraction method, the dried material is then exposed to a crosslinking agent. The crosslinking agent can be provided as a solution or in a gas phase to form a crosslinked porous body. The solvent used in forming a solution of crosslinking  
35 agent can vary widely. Such a solvent or gas acts as a

carrier vehicle for the crosslinking agent. Obviously,  
the carrier vehicle should be inert to the gel material  
and capable of solubilizing the crosslinking agent.  
The supercritical fluid extraction method may be a  
preferable procedure for making materials of very low  
density materials, i.e. less than about 0.05 grams per  
cc.

After the solvent exchange or alternative  
procedure for the solvent exchange is the crosslinking  
material. The choice of gel-forming agent will vary  
with the selection of crosslinking material. Similarly,  
the amount of crosslinking agent will vary with the  
amount of gel-forming material present in the set gel  
and the amount of crosslinking agent will vary with the  
functional groups present in the polymer backbone of  
the gel-forming material. Basically, any number of  
well-known chemical crosslinking agents can be selected  
for use in the crosslinking step. Illustrative of a  
crosslinking agent is the use of a diamine or polyamine  
as linkers for crosslinking hydroxyl and/or carboxylic  
moieties along a polymer backbone. For the purposes of  
this invention, often used are diisocyanate compounds,  
such as 2,4-tolylene diisocyanate. Aromatic diisocyanates,  
addition to aliphatic and aromatic diisocyanate, are preferred. In  
crosslinking agent, many other compounds might find use  
such as epichlorohydrin, aldehydes and dialdehydes,  
trimetaphosphates, vinyl sulfones, urea-formaldehyde  
systems and, di-halogenated aliphatics. Specific  
compounds include bis(hydroxymethyl)ethylene urea,

N,N'-methylenebisacrylamide, 1,3,5-trichloro- and 1,3,5-triacryl s-triazine.

The final step of the process is to isolate the crosslinked polymer body from the crosslinking solvent.

5 The fluid phase of the gel can be removed by a variety of techniques. A mixture of crosslinking solvent, any remaining unused crosslinking agent or side products of the crosslinking reaction may be simply drained from the solid crosslinked product. The reaction mixture  
10 containing the crosslinking solvent can also be removed by subjecting the crosslinked material to a vacuum step. Preferably, the solid crosslinked material that results from a crosslinking step is isolated and dried within a vacuum oven at a temperature of at least 20°C  
15 at a vacuum at least about 10 to 50 lbs. vacuum. The drying conditions are selected in order to effect rapid evaporation of any leftover solvents or volatile crosslinking agents inside the crosslinked gel body.

One of the additional advantages of the porous bodies of this invention and articles formed therefrom is the diversity of chemical modification which can be performed on the gel-forming prior to, during or after isolating the open-celled porous cross-linked body.

The gel-forming materials have functional groups, such 25 as -OH, -COOH, -OSO<sub>3</sub>, and -NH<sub>2</sub> which can be chemically modified by conventional reagents in the art. The number of functional groups which can be derivatized by chemical modification depends on the number of functional groups of the gel-forming material which are  
30 involved in the crosslinking. With less crosslinking, additional functional groups can be available for a desired chemical modification. The numerous modifications which can be performed on the functional groups of a gel-forming material make the range of  
35 applications for the porous bodies and articles of this

invention almost endless. The articles can be modified  
for storage and transport of chemicals, for specific  
support applications, e.g. catalytic reactions or  
filter media, for insulation applications and for  
separation techniques. Alginic acid contains a  
substantial number of carboxyl groups, and chitosan  
contains a significant amount of free amine groups,  
both which are easily derivatized by numerous reagents.  
Both materials also contain abundant hydroxyl groups,  
which are available for chemical modification. Even if  
one crosslinks these materials using hydroxyl-specific  
reagents such as diisocyanates, sufficient free  
hydroxyls can survive the process intact and should be  
accessible for further reaction.

An additional embodiment of the invention relates  
to a method for the removal of one or more materials  
from a fluid stream comprising contacting the fluid  
stream with one or more of the porous bodies of this  
invention. Inorganic or organic materials can be  
removed. The porous bodies can be of any desired shape  
which is desired for a particular application.

One of the novel methods of this invention relates  
to a method for the removal of one or more metals from  
a fluid stream containing the metal or metals, which  
process comprises contacting said fluid stream  
containing one or more metals with one or more porous  
bodies of this invention. The methods for removal of  
metals provides an efficient technique for the removal of  
radioactive metals, including precious metals and  
heavy metals, such as uranium. The porous bodies  
can be placed in a vessel having an inlet and outlet  
means allowing for the inflow and outflow of a fluid  
stream.

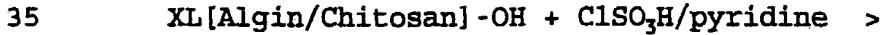
The porous bodies can be loaded (placed) in a  
vessel, which may be an open flow-through column or a

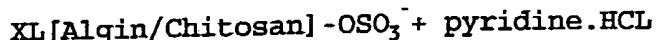
closed reactor, in any conventional manner. They can be used in a stirred tank reactor, fixed bed reactor or fluidized bed reactor. These types of reactors are well-known in the art. Hydrogels, such as sodium 5 alginate and chitosan are known for their ability to bind metals. Normally, physical properties of these materials prevent their convenient implantation in metal remediation of aqueous wastestreams. However, when the gels are formed into porous bodies as 10 described in this invention, they possess a physical form suitable to any type of column or reactor.

Novel methods of this invention relates to a method for the recovery of one or more metals from a fluid stream containing the metal or metals, which 15 process comprises contacting said fluid stream containing one or more metals with one or more porous bodies of this invention and recovering the one or more metals. Recovery of the metals from the porous bodies can be accomplished by conventional means in the art.

20 Metals can be separated from the porous bodies by passing a solution over the porus bodies which causes the metals to detach from the porus bodies. The metals can be removed together or selectively by varying the pH of the recovery solution. The methods for removal 25 of metals provides an efficient technique for the recovery of heavy metals, including precious metals and radioactive metals, such as uranium.

One application is the use of the materials of this invention as ion-exchange resins. For example, a 30 porous body derived from chitosan or alginate can be converted to a cation exchange resin by derivatizing free hydroxyl groups with chlorosulfonic acid/dry pyridine to yield the following derivative:



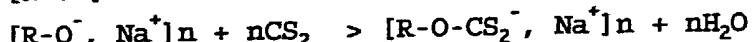
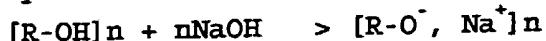


wherein XL = crosslinked

Another example would involve the addition of a  
5 phosphate ester across free hydroxyl groups in alginic  
or chitosan, using phosphorus oxychloride/pyridine:



Algin or chitosan xanthates may also be prepared  
by the reaction of crosslinked material with carbon  
disulfide in a concentrated solution of sodium  
15 hydroxide:



wherein R is a gel-forming material having  
plurality of OH groups.

20 These derivatization chemistries only serve to  
point out the varied possibilities for introducing ion-  
exchange capacity. Many different chemistries for  
making anionic/cationic ion-complexing resins are well-  
known in the art as well as other derivatization  
25 chemistries for other applications.

Alternatively, one could couple a polymer which  
possesses additional functional groups to the porous  
body and then derivatize these functional groups as  
described above. In this way, one could substantially  
30 increase the versatility of the porous body to perform  
a desired function.

The backbone of the gel-forming material can also  
be derivatized in a myriad of other ways. For example,  
the hydrophobic/hydrophilic index of the material can  
35 be altered by derivatization of available hydroxyl

groups with a hydrophobic or hydrophilic compound. For example derivatizing hydroxyl groups with phenyl isocyanate would yield a more hydrophobic material than the unmodified crosslinked gel.

5       The crosslinked porous materials of this invention can also be used as a carrier or support matrix for active agents. An active agent is a natural or synthetic material which has an activity to perform a reaction or function. Active agents can be added at  
10      any time during the preparation of the crosslinked porous body or after preparation of the porous body, e.g. as a coating. In preferred embodiments, the active agent is mixed with a selected gel-forming material without a substantial loss of its activities, and the  
15      combined composition is then gelled and crosslinked pursuant to the process of this invention. The active agent within the crosslinked porous body can then be used in applications where the properties of the porous body, such as strength, porosity or low density, are needed.  
20      Illustrative of active agents which have limited use because of their physical attributes are various biologically derived materials, which are either whole cells or fractions thereof, that possess the ability to sequester various metals with unexpected  
25      selectivity and capacity. A drawback has always been the physical form of these materials; either they were in powdered form or in the form of a gelatinous mass. One can put these complexing agents into a useful form so as to serve a practical industrial function by  
30      entrapment within and/or attachment on the gel-forming materials.

35      The crosslinked porous bodies of this invention, whether modified or not, have low density and other excellent physical characteristics, such as a desirable pore volume and/or pore size. Practically, this means

that there is a great deal of empty space within the material which can be utilized to hold or contain other materials which can be added to it. A factor which renders this property of great commercial interest is 5 that, despite their low density and useable internal volume, the crosslinked have beneficial strength characteristics. One way to exploit the unusual properties of the porous bodies of this invention is to use the empty space for absorption of materials. For 10 example, the porous body can be impregnated with the an active agent to facilitate and/or enhance the absorption of a desired material.

Another way that crosslinked porous bodies of this invention can be employed is to introduce additives, 15 such as antibacterials, plasticizers, stabilizers, antioxidants, etc., into plastics materials by adding these additives within a crosslinked gel as microcapsules. Currently, plastic additives are physically mixed into precursor materials at some point 20 during the processing. The net effect of this is to weaken the modulus of the polymer material because of mitigation of the structural components of the mixture. This loss in strength requires that structural fillers and reinforcements also be added to make up for the 25 weakening effects of the additives. By loading the porous body with additives to form microcapsules, and adding these microcapsules to the plastics precursors, the overall weakening effects of the addition the additives should be much less than when the additives 30 are added directly since the additives enclosed within the microcapsule are segregated from the structural components of the plastic. Furthermore, the microcapsule can be modified to control the release of specific amount of additive, thereby increasing the 35 useable lifespan of the plastic. One limitation of

most plastics is that when the additives are exhausted from them, due to migration to the surface and loss, the plastic loses the properties conferred onto it by that additive. Thus, plastics can be improved by 5 controlling the rate of loss of an additive, such as an antioxidant or plasticizer.

Compositions with enhanced capacity and/or selectivity for a metal or metals may be formed by adding active agents which are metallophilic materials 10 to the gel-forming compositions. Metallophilic as used herein refers to materials having a beneficial metal-binding ability. These metallophilic materials may be naturally-occurring biological materials or synthetic compounds known in the art for use in metal removal and 15 recovery, such as oximes. Preferably, the metallophilic materials possess a metal-binding ability which is sufficient to remove the metal or metals from a desired fluid stream. In preferred embodiments, the metallophilic materials are naturally-occurring 20 biological materials. Compositions comprising naturally-occurring biological materials and at least one porous body of this invention are referred to as biocompositions. A wide range of biocompositions can be made by incorporating bioactive materials into the 25 alginate/chitosan crosslinking mixture. Illustrative of such materials are activated sludge, blue-green algae, tannic acid, humic acid, and other biological materials. Such materials can be mixed in with a gel-forming material. The gels are then solvent exchanged 30 and chemically crosslinked essentially as previously described. By carefully selecting additive components in this way, a family of new bioabsorbents tailored to the efficient treatment of specific metal-bearing wastestreams can be introduced.

35 Another field for application of the materials of

this invention is carbonization. Natural gas is a clean energy source, which is abundant in this country. One factor which precludes its use as a fuel for automobile engines, and other engines which currently 5 use petroleum-based fuels, is difficulty in the safe storage and transport of the gas. It has been found that carbonization of certain polymers produces materials which adsorb or immobilize natural gas. The gas, when adsorbed onto solid carbon materials, is much 10 less hazardous, and it's even feasible to consider the use of adsorbed natural gas to power motorized vehicles. Unmodified or modified forms of the crosslinked porous bodies of this invention can also absorb and deliver natural gas.

15 The crosslinked gel of this invention can also be used as templates. If the crosslinked gel has a physical limitation in view of a particular use, a template application may be used to incorporate beneficial properties of the crosslinked gel into 20 another material. For example, the gel can be used as a template onto which a layer of inert inorganic material of superior strength or heat resistance may be deposited. After deposition of the inorganic crust, then the gel template may be etched away, or chemically 25 digested for removal, leaving a 'casting' of inorganic material which retains the pore characteristics and large surface area of the original template. One template technique is noted as follows: 1) polymerize styrene onto the inner surfaces of crosslinked hydrogel, in effect forming a skin impression of all the pores and surfaces of the template, 2) deposit a layer 30 of carbon onto the styrene polymer, 3) silanize the carbon layer and heat slowly to about 300 C. This should form a layer of silicon carbide, even at this 35 low temperature. The crosslinked polysaccharide can

then be acid etched away, or chemically digested with peroxides, etc. Silicon carbide is an extremely strong material, which can serve as an excellent catalyst support. The high surface area properties of the  
5 template crosslinked hydrogel, combined with its ease of removability, make these materials ideal candidates for use as templates. The following examples are merely illustrative of our invention and should not be considered limiting in any way.

10

Procedures for Measuring Properties of the Materials

Surface areas were determined by nitrogen adsorption. Samples were first degassed for 16 hours in a helium atmosphere at 50°C. Adsorption/desorption  
15 measurements were made on a Quantasorb sorption systems, a continuous flow gas chromatographic instrument, manufactured by Quantachrome Corp., Syosset, NY. Values reported are based on single point measurements at liquid nitrogen temperature, 78K, and  
20 0.3 partial pressure of nitrogen in helium with a total flow rate of 20 cm<sup>3</sup>/min. The surface areas were calculated using the BET (Brunauer, Emmett and Teller) isotherm following the procedure recommended by the equipment manufacturer.

25

The apparent bulk density, pore volume and average pore diameter were determined by mercury porosimetry. Samples were first degassed for 16 hours in a helium atmosphere at 50°C. Measurements were made on a Autopore 9210 mercury porosimeter manufactured by  
30 Micromeretics, Norcross, GA. Measurements were taken over the pressure range 20 to 60,000 lb/in<sup>2</sup> (138,000 to 410,000,000 Pa) at 60 points with roughly equal logarithmical spacing. Pressures are converted to pore diameters via the Washburn equation where the surface  
35 tension of mercury, 485 dyne/cm, and the contact angle,

140°, are assumed. The corresponding pore diameters go from 10  $\mu\text{m}$  to 3.6 nm. The apparent bulk density is measured at 20 lb/in<sup>2</sup> (138,000 Pa). The pore volume includes those pores filled as the pressure changes over the range of the experiment. The average pore diameter is defined as four times the ratio of the pore volume to the total pore area, where the pore surface for pores of a given diameter is calculated from the incremental pore volume assuming cylindrical shape.

5 Procedures followed for operation and analysis were those recommended by the manufacturer of the porosimeter.

10 Generally, the procedure used for determination of compressive properties of the crosslinked materials is that described in the 1982 ANNUAL BOOK OF ASTM STANDARDS; Part 36, Plastics- Materials, Film, Reinforced and Cellular Plastics; High Modulus Fibers and Composites: pp. 169-172, ASTM Designation: D 1621 - 73 (Reapproved 1979): ASTM, Philadelphia, PA. This 15 procedure provides information regarding the behavior of rigid cellular materials under compressive loads. Deformation data can be obtained, and from a complete load-deformation curve it is possible to compute the compressive stress at any load, and to compute the 20 effective modulus of elasticity. The procedure is described briefly, as follows: Cubes of crosslinked material were measured in all dimensions to an accuracy of +/- 1%, and placed between the mounting plates of a Universal Instron Machine. A load was applied to the 25 specimen in such a manner that it was uniformly distributed over the entire loading surface of the specimen. The rate of crosshead (deflection) movement was 0.1 +/- 0.01 in./min. As loading pressure was applied, specimen deformation was measured, and the 30 amount of deformation was recorded using an automatic 35

recorder. The resulting compressive stress-strain diagram, in which values of compressive stress are plotted as ordinates against corresponding values of compressive strain as abscissas, were used to describe 5 the compressive properties of the crosslinked materials disclosed herein.

EXAMPLE 1

1. PREPARATION OF A POROUS BODY (MATRIX)  
10 FROM CROSSLINKED ALGINATE

Five grams of sodium alginate were added to 100 ml distilled water to yield a 5% solution. After addition of the sodium alginate, the solution was allowed to hydrate for 16 hrs. The fully hydrated polymer was 15 then centrifuged to eliminate air bubbles. The viscous solution was exposed to a 0.2M calcium chloride solution to set or coagulate into a gel. Following completion of the setting step, the gel was cut into cubes of about 1 cc volume and then calcium alginate 20 cubes were then washed thoroughly in water to remove excess calcium chloride and the calcium alginate cubes were exposed to a solution comprised of 25% acetone in distilled water (v/v). After equilibration, the 25% acetone water solution was decanted and replaced with a 25 50% acetone/water solution. The 50% acetone/water solution was decanted after equilibration and replaced with 75% acetone/water. Following equilibration in this solvent mixture, the solvent mixture was replaced with 100% acetone. The cubes were then equilibrated 30 in 100% toluene, and crosslinked by the addition of 3.3 ml of 2,4-tolylene diisocyanate (TDI). Triethylamine was added as a base catalyst. The solution was heated to 100-110°C, and allowed to react for about 16 hrs. Following crosslinking, the material was 35 washed in fresh toluene and dried in a vacuum oven.

The following table lists various physical properties of the final product.

PROPERTIES OF THE CROSSLINKED ALGINATE

5	Apparent Bulk Density	0.164 g/cc
	Surface Area	380 m <sup>2</sup> /g
	Pore Volume	2.97 cc/g
	Average Pore Diameter	365 Angstroms
	Compressibility	10% yield at 347 psi

10

EXAMPLE 2

**PREPARATION OF A POROUS BODY FROM CROSSLINKED  
CROSSLINKED ALGINATE (Scale-up)**

30 grams of high viscosity sodium alginate were  
15 added to 600 ml distilled water. The viscous 5% Sodium  
alginate solution was allowed to hydrate for 16 hr.  
The solution was then centrifuged at 2000 RPM for 30  
min to remove air bubbles. Calcium chloride solution  
20 (0.2 M) was then poured over the viscous hydrocolloid  
solution to form the gel. The gel was allowed to set  
for 16 hr., and the fully set gel was then sliced into  
cubes of approximately 1 cc volume. The cubes were  
then washed and solvent exchanged as described in  
Example 1. The exchanged material was crosslinked with  
25 20 ml of 2,4 -tolylene diisocyanate in the presence of  
a catalytic amount of triethylamine. Crosslinking was  
performed at a temperature of 100 -110°C, as described  
in Example 1. Following crosslinking, the material was  
washed in fresh toluene, and dried in a vacuum oven.  
30 The apparent bulk density and surface area of the final  
material was then determined.

EXAMPLE 3**PREPARATION OF A POROUS BODY FROM CROSSLINKED CHITOSAN**

5 grams of chitosan flakes were dissolved in a solution of dilute acetic acid (96 ml distilled water + 5 3.75 ml glacial acetic acid). The flakes were allowed to fully hydrate, and the viscous solution was centrifuged to remove air bubbles. The gel was then made by contacting the viscous hydrocolloid with a solution of 10% (w/w) sodium hydroxide for 24 hr. The 10 gel was then sliced and washed in distilled water to remove excess NaOH solution. The washed slices were then solvent exchanged into toluene as described in Example 1, and crosslinked with 2,4-TDI as described above. The crosslinked product was then dried in a 15 vacuum oven, and ground to a powder (40 mesh or less). The table below lists the physical properties of the final product.

PROPERTIES OF CROSSLINKED CHITOSAN

20	Apparent Bulk Density .....	0.0877 g/cc
	Surface Area .....	364 m <sup>2</sup> /g
	Pore Volume .....	4.386 cc/g

EXAMPLE 4

25       **OPTIMIZATION OF THE SOLVENT EXCHANGE PROCEDURE  
USED TO PRODUCE LOW-DENSITY POROUS BODIES  
FROM CROSSLINKED HYDROGELS**

In order to optimally crosslink hydrogel materials with many suitable industrial crosslinking agents, the 30 water in the initial hydrogel is replaced with a crosslinking solvent. We have chosen toluene as a suitable representative crosslinking solvent. Prior to replacing the water with toluene or another crosslinking solvent, it is often advantageous to 35 replace the water with an intermediate solvent which is

aprotic and has a surface tension less than that of water and above that of the crosslinking solvent.

Acetone was selected as an intermediate solvent. It is observed that abrupt exposure of a hydrogel to high acetone concentrations resulted in partial shrinking of the gel, which should be avoided to maintain a low density material. In order to minimize solvent use without substantially shrinkage the gel, the maximum step-size increase in concentration of intermediate solvent (in water) sustainable by the gel without collapse had to be determined. This was done by making four crosslinked gels using the same materials except that different concentration gradients were used to achieve the replacement of water with pure acetone.

For an example, the water of the hydrogel was replaced directly with pure acetone (100%). In the other three samples, concentration gradients of 10%, 25% and 50% were used. For each gradient, the concentration of intermediate solvent (acetone) in the hydrogel was increased incrementally to 100%, e.g. nine equal incremental steps from 10% acetone in water to reach 100% acetone in the gel. To assess gel shrinkage, the initial pellet diameters of a representative population ( $n = 10$ ) were measured, and the pellets were then exposed to the next step up in acetone concentration. The pellet diameters were remeasured after a 15 minute equilibration period and the process was repeated until the pellets were in 100% acetone. Finally, the pellets were placed directly into 100% toluene (the final solvent for crosslinking), or washed further with fresh acetone before exposure to toluene. The results shown in the Figure 4, indicated an unambiguous relationship between step-size and gel shrinkage. Exposing the pellets directly to 100% acetone resulted in a greater than 60% reduction in volume. Taking the acetone

concentration to 100% in two steps (50%/step) resulted in less than about than 25 shrinkage. About 24% shrinkage was observed in pellets taken to 100% acetone in four steps (25% step); whereas increasing the 5 acetone to 100% in ten steps (10% each step) resulted in only about 20% shrinkage of the gel. Furthermore, it was found that the pellets could be exposed directly to 100% toluene with little additional shrinkage. The complete changeover to acetone, therefore, may be 10 effected in as little as four incremental steps (25% acetone/water, 50% acetone/water, 75% acetone/water, 100% acetone). This stepwise solvent exchange results in a practical approach to minimize solvent use. Also, since the exchanges are carried out in a batch format, 15 spent wash solutions may be reused for subsequent exchanges. These results are important because they mean that complete exchange from water to toluene may be performed using minimal solvent quantities, and without generating enormous amounts of organic solvent 20 waste.

EXAMPLE 5

**PREPARATION OF ULTRA-LOW DENSITY POROUS  
BODY FROM CROSSLINKED ALGINATE**

25 A 0.25% solution of sodium alginate was fully hydrated in 100 ml of distilled water. The hydrated solution (pre-gel) was then transferred to a syringe and centrifuged to eliminate air voids within the gel. The pre-gel was then introduce drop-wise into a 30 solution of 0.2 M calcium chloride, and the resulting pellets were allowed to coagulate. The calcium solution was then decanted, and the calcium alginate pellets were washed in a large excess of distilled water to remove excess calcium chloride solution. 35 Following the wash step, the pellets were solvent

exchanged to toluene, and crosslinked with 2,4-TDI as described in Example 1. The pellets were then freeze dried by transferring the pellets to freeze drying flasks, freezing at -20°C and then lyophilizing for 5 about 12 to 16 hours. The density, surface area and pore characteristics were measured.

PROPERTIES OF ULTRA-LOW DENSITY CROSSLINKED  
ALGINATE

10

Apparent Bulk Density ..... 0.042 g/cc

Surface Area ..... 200 m<sup>2</sup>/g

15

Pore Volume ..... 2.917 cc/g

Pore Area ..... 226 m<sup>2</sup>/g

Average Pore Diameter ..... 517 Angstroms

20

EXAMPLE 6

PREPARATION OF CROSSLINKED ALGINATE USING A  
QUICK-COOLING TECHNIQUE TO SET THE INITIAL GEL

25

Fifty milligrams of sodium alginate were added to 10 ml of 58% ethylene glycol in water, and the mixture was allowed to gel. The fully hydrated gel was then extruded dropwise into 100 ml of precooled acetone 30 (-40°C, on dry ice). The rapid transition to this temperature caused the alginate gel to become rigid, but the gel did not freeze because of the ethylene glycol in the gel mixture. The extruded pellets were allowed to stir for about 1/2 hour in the cold acetone, 35 and then the wet acetone was decanted and the pellets

were transferred to a 100 ml pear-bottom flask containing 80 ml of pre-cooled, dry acetone, kept under nitrogen. The flask was allowed to warm to about 22°C and then the gel was crosslinked with two additions of 5 molar excess of 2,4-TDI. The final bulk density of the dried material was about 0.028 g/cc.

EXAMPLE 7

PREPARATION OF CROSSLINKED ALGINATE USING  
10 DILUTE ORGANIC ACID AS A GELLING AGENT

A 2% sodium alginate solution (12ml) was extruded dropwise into 200 ml of 10% acetic acid (v/v). The pellets were allowed to set overnight, washed with water to remove excess acetic acid, and then subjected 15 to the solvent exchange and TDI crosslinking procedures described above. The pellets were freeze-dried overnight, as noted in Example 5, and the final bulk density of the unground pellets was about 0.031 g/cc.

Other organic acids capable of gelling the sodium 20 alginate include adipic and formic; however, a simple mineral acid such as HCl had the opposite effect of substantially destroying the gel completely.

25 EXAMPLE 8

EFFECT OF INITIAL GEL CONCENTRATION ON THE  
FINAL DENSITY OF THE CROSSLINKED MATERIAL

The effect of the initial gel concentration on the final density of crosslinked material was determined by 30 preparing a series of gels of increasing concentration, and comparing the densities of the final dried, crosslinked products. Gels were prepared with initial concentrations of 0.25%, 0.5%, 1.0% and 2.0% (w/v) were prepared. The gels were set as pellets by dropwise 35 introduction into a solution of 0.2 M CaCl<sub>2</sub>, generally

as described in Example 5. The calcium alginate pellets were then solvent exchanged and crosslinked with 2,4-TDI as described in Example 1. Following crosslinking, the reaction solution was decanted, and  
5 the pellets were dried. The dried materials were then ground to a particle size of less than about .20 mesh and the apparent bulk densities (ABD) were measured. As can be seen in Figure 5, the final ABD of a given material was highly dependent upon the concentration of  
10 the starting gel from which it was made. The significance of these findings is that the final density of a material can be controlled by selecting an initial gel concentration which will yield the desired density.

15

EXAMPLE 9

RELATIONSHIP BETWEEN DENSITY AND PORE  
SIZE OF THE POROUS BODIES FORMED FROM CROSSLINKED GELS

Mercury porosimetry was performed on the same four samples described in the preceding example. The intent was to determine whether or not a relationship existed between the final ABD of crosslinked alginate and the average pore diameter of the material. As can be seen in Figure 6, such a relationship does exist. As the  
20 apparent bulk density decreases, the average pore diameter is seen to increase, within the ranges investigated. These results imply one would be able to, within limits, control the pore diameter of the final crosslinked material. For example, if a specific  
25 application requires pore diameters in the 200 - 300 angstrom range (ideal for immobilized enzyme supports), then one could process gels of the appropriate initial concentrations to yield a final product with a final  
30 density of about 0.15 g/cc or greater.

35

EXAMPLE 10**RELATIONSHIP BETWEEN DENSITY AND SURFACE AREA  
OF POROUS BODIES FORMED FROM CROSSLINKED BIOHYDROGELS**

The surface area of several crosslinked alginate samples of varying densities was measured in order to determine if there was a definable relationship between surface area and density. As can be seen in Figure 7, a relationship between ABD and surface area exists.

5 The data points arrayed along the two lines (solid and dashed) represent two families of materials which had different processing conditions. The samples along the solid (lower) line were processed as pellets, and were freeze-dried after crosslinking with 2,4-TDI. The data points along the dotted (upper) line were

10 processed as cubes and were dried in a vacuum oven. For a specific application, material with a minimum surface area of, say,  $300 \text{ m}^2/\text{g}$  may be required. By careful selection of initial gel concentration and processing technique, then, it is possible to produce

15 material with a surface area in this desired range.

20

EXAMPLE 11**UTILITY OF VARIOUS NATURALLY-DERIVED HYDROGELS  
FOR THE PRODUCT OF CROSSLINKED GELS**

25 Various naturally-derived hydrogels were tested for their ability to form low-density crosslinked materials. The following materials were tested; Sodium Alginate, Chitosan, Agar, Carrageenan, Locust Bean Gum, Guar Gum, Gum Arabic, Gum Ghatti, Pectin, Tragacanth, 30 and Xanthan Gum. Dissolving Gums Arabic, Ghatti, Tragacanth and Xanthan in distilled water resulted in the formation viscous solutions, but no good gelling procedure was found for any of them. Pectin was gelled using the following procedure: To 100 ml distilled 35 water was added 5 g of pectin, 3 g of  $\text{CaCl}_2$ , and 0.2 g

of citric acid. The mixture was heated slowly to 80°C, and allowed to cool to room temperature. The pectin gel that resulted was not sufficiently strong to be useful. 5% Na-alginate solution was set in 0.2 M 5 CaCl<sub>2</sub>, and 5% chitosan was gelled in dilute acetic acid (Ca. 4% w/w) and then set in 10% NaOH (w/w). 5% mixtures of agar in water and carrageen in water were heated to about 100°C, and then allowed to cool to set into a stiff gels. 5% solutions of guar and locust bean 10 gum were prepared, and then set with sodium borate solution. Following gelling, the gels were sliced into cubes of approximately 1 cc<sup>3</sup> volume. The cubes were then subjected to the solvent exchange and crosslinking procedures described in Example 1, and then dried. To 15 assess the utility, of the various materials, their net shrinkage was measured. Shrinkage was used as a criterion, since as the materials shrink they densify. Therefore, the dimensions of a statistically representative population of the starting cubes (n = 5) 20 were measured using a micrometer, and the dimensions were remeasured after the solvent exchange procedure, after the crosslinking procedure, and after the final drying. As can be seen in Figure 8, the chitosan and sodium alginate show superior properties. The agar and 25 carrageenan displayed minimal shrinkage during the solvent exchange procedure. However, upon drying, these two collapsed to a fraction of their initial volumes. The locust bean and guar gum samples collapsed with the initial solvent exchange procedure. 30 The fact that the agar and carrageenan did not collapse during the solvent exchange procedure also makes them viable candidates for other crosslinking procedures.

COMPARATIVE EXAMPLE

Using the chitosan crosslinking procedure disclosed in Kokai Patent Publication No. 133143-1986, "Heavy Metal Adsorbing Agent", a sample was prepared.

5 A material was prepared as described in example 1 of this publication. Shrinkage of the material produced using their protocol was used as a guide to assess collapse of the material. The degree of collapse of their material was compared to those values  
10 obtained using our procedures in order to determine the relative performance of the two procedures.

Chitosan, was mixed with dilute acid, such as formic or acetic, makes a gel and then placed in a solution of sodium hydroxide, which coagulates the  
15 chitosan to form an opaque, friable material. The coagulated chitosan pellets are placed directly into acetone, and after washing with fresh acetone, added 2,4-tolyene diisocyanate to effect the crosslinking.  
The chitosan pellets shrank during the initial exposure  
20 to acetone. The initial diameters of 20 pellets were measured using a micrometer, and the pellets were remeasured after drying the pellets. The pellets went from an average initial diameter of 2.27 mm to only 1.457 mm after drying, a loss of 57.5% in diameter.  
25 Using the procedure of our Example 1 procedure, however, the loss was only about 3.3%.

EXAMPLE 12

BINDING OF VARIOUS METALS TO THE CROSSLINKED ALGINATE  
30 MATRIX (i.e. POROUS BODY)

Binding of Cd(II), Ni(II), Pb(II), Cu(II) and Cr(III) at varying levels in a mixed-metal aqueous environment.

35 A 2% (w/v) solution of sodium alginate in

distilled water was prepared and allowed to fully hydrate for a period of about 16 hours. The sodium alginate solution was then loaded into a syringe and the viscous solution was introduced dropwise into a  
5 beaker containing 0.2 M  $\text{CaCl}_2$ . The pellets were allowed to set in the  $\text{CaCl}_2$  solution for at least 16 Hr, and were then washed in distilled water in order to remove excess  $\text{CaCl}_2$ . The calcium alginate pellets were then solvent exchanged and crosslinked with 2,4-TDI,  
10 essentially as described in EXAMPLE 1. The crosslinked pellets were washed with fresh toluene, and dried in a vacuum oven at 50 C. The dried pellets were then ground using a Wiley bench mill to a particle size sufficiently small to pass through a 40 mesh screen.  
15 The ground alginate crosslinked matrix was then used for the metal binding studies described below.

Fifty milligrams of ground, crosslinked alginate matrix was weighed into each of 6 test tubes (16 mm by 100 mm). The sorbent matrices were initially pre-wet  
20 with 5 ml methanol, and then washed twice with 10 ml of distilled water. Mixed-metal solutions were prepared containing 10 ppm, 100 ppm and 1000 ppm of each of the following metals: Cd(II), Ni(II), Pb(II), Cu(II) and Cr(III). Each mixed-metal solution was adjusted to a  
25 pH of 3.6 with dilute nitric acid and then filtered before use in the metal binding assays. Ten ml of each mixed-metal solution was added, in duplicate, to test tubes containing the pre-wet, washed sorbent matrix. A small magnetic stir bar was then added to each tube and  
30 the contact mixtures were incubated with stirring for 2 hrs. At the end of the contact period, all the tubes were centrifuged to pellet the sorbent matrices, and the supernatants were carefully removed using Pasteur pipettes. The supernatants were then assayed for Cd,  
35 Ni, Pb, Cu and Cr by atomic absorption spectroscopy

(AAS). The pellets were digested by acid hydrolysis and the level of each metal in the pellets was determined by AAS. The mixed-metal standard solutions were also assayed by AAS to verify the initial concentration of each metal.

Figure 9 shows the mean values from duplicate analyses of each metal found in the supernatants (crosshatched) and in the pellets (solid) following exposure at the 10, 100 and 1000 ppm levels. As can be seen in this figure, total metal recovery was very good; in most cases at least 95% of the total metal added to the contact mixtures was recovered in the combined pellet and supernatant fractions. Only in one case, Cr(III) at the 100 ppm level, was less than 90% recovery obtained. Following the 2 Hr exposure of the crosslinked alginate matrix to the 10 ppm level, 95 - 100% of all the metals, except Ni, was found to be bound to the pellet fraction. In the case of Ni, 81% of the metal was recovered in the pellet. Essentially all the Pb added at the 100 ppm level was found in the pellet (bound) fraction. The sorbent was found to bind about 70% of the Cu, 50% of the Cd and Cr, and about 20% of the Ni added at this intermediate level. Following exposure at the 1000 ppm level, about 50% of the Pb, 20% of the Cr, 11% of the Cu, 7.5% of the Cd, and about 4% of the Ni was recovered in the bound fraction. The total amount of all metals bound following exposure at the 1000 ppm level was about 9.25 mg, or about 18.5% of the sorbent weight. The amount of each metal bound at the 1000 ppm exposure level, expressed in mg of metal bound per gram of sorbent was as follows: 96 mg/g, Pb; 45.4 mg/g, Cr; 21.8 mg/g, Cu; 14.4 mg/g, Cd; and 7.5 mg/g, Ni. The number of moles of each metal bound following exposure at the 1000 ppm level was as follows: 43.5 Umoles of Cr; 23.1 umoles

of Pb; 17.2 umoles of Cu; and about 6.4 umoles each of Cd and Ni.

EXAMPLE 13

5     **BINDING OF VARIOUS METALS TO THE CROSSLINKED CHITOSAN  
MATRIX (POROUS BODY)**

Binding of Cd(II), Ni(II), Pb(II), Cu(II) and Cr(II,  
III) in a mixed-metal aqueous environment by  
10 crosslinked chitosan matrix.

A 2% (w/v) solution of chitosan-acetate in  
distilled water was prepared and allowed to fully  
hydrate. The solution was then introduced dropwise  
15 into a solution containing 10% NaOH, resulting in the  
formation of pellets of the set gel. The pellets were  
washed in distilled water, and exchanged to toluene and  
crosslinked with 2,4-TDI, essentially as described in  
EXAMPLE 3. The crosslinked pellets were then dried,  
20 ground to 40-mesh particles, pre-wet, and washed as  
described in EXAMPLE 12.

A mixed-metal solution was prepared containing 10 ppm  
of each of the following metals: Cd(II), Ni(II),  
Pb(II), Cu(II) and Cr(II, III). The solution  
25 containing all these metals was then adjusted to a pH  
of 5.4 - 5.5, and was filtered before use. The metal  
binding experiment was performed essentially as  
described in EXAMPLE 12.

Figure 11 shows the mean values from the duplicate  
30 analyses of each metal found in the supernatants  
(crosshatched) and in the pellets (solid) following  
exposure to the mixed-metal solution. Generally,  
greater than 95% of the added metals could be accounted  
for in the combined supernatant and pellet fractions of  
35 the contact mixtures. All of the recovered Cr and Cu

was found bound to the sorbent. About 90% of the recovered Pb and 45-47% of the Cd and Ni was also found bound to the pellet fraction.

5

EXAMPLE 14**BINDING OF URANIUM TO THE CROSSLINKED ALGINATE MATRIX**

10

Eight 50 mg samples of ground, crosslinked alginic acid, prepared from a 5% calcium alginate gel as described in EXAMPLE 1, were wetted with methanol and washed with distilled water as described in EXAMPLE 12. 15 Standard solutions containing 105 ppm, 251 ppm, 472 ppm and 916 ppm Uranium were prepared from a stock solution containing 975 ppm Uranium (as Uranyl Nitrate). These solutions were adjusted to a pH of 3.9 - 4.0 before use. 100 ml of each solution were added, in duplicate, 20 to the pre-wetted, washed crosslinked alginic acid sorbent, and incubated at room temperature (about 24°C) with stirring for 2 Hr. At the end of the 2 Hr. equilibration contact period, the supernatants were analyzed for Uranium content by inductively coupled 25 argon plasma emission spectroscopy (ICP), and binding to the sorbent was calculated by difference. Concurrent controls, consisting of Uranium standard solutions in vessels containing no sorbent, were also processed side-by-side with the experimental samples to 30 verify that no background binding occurred.

Results of the Uranium binding experiment are presented in the table below. The figures shown are the mean values from the two observations at each exposure level. Even at the relatively low exposure 35 level of 105 ppm, binding of greater than 187 mg

Uranium bound per gram of sorbent was observed. The maximum observed capacity, nearly 280 mg Uranium bound per gram of sorbent or about 28% by weight, was seen at the highest (916 ppm) exposure level.

5

#### URANIUM UPTAKE CAPACITY OF THE CROSSLINKED MATRIX

10	INITIAL	SOLUTION	CAPACITY	
	EXPOSURE	EQUILIBRIUM		
	<u>LEVEL (PPM)</u>	<u>CONCENTRATION (PPM)</u>	<u>BOUND (MG)</u>	<u>MG BOUND/G SORBENT</u>
	105	10.7	94.3	187.3
	251	125	126	250
	472	369	103	204.2
15	916	776.5	139.5	279.8

#### EXAMPLE 15

##### 20 USE OF ACTIVE METAL-BINDING AGENTS IMMOBILIZED WITHIN THE CROSSLINKED MATRIX FOR METAL RECOVERY.

Humic acid and tannic acid, natural materials of known metal binding ability, were selected for immobilization within an alginate crosslinked matrix. A 2% (w/v) solution of sodium alginate in distilled water was made and allowed to fully hydrate. Two grams of humic acid were added to 100 ml of the 2% sodium alginate solution, and two grams of tannic acid were added to another 100 ml of 2% sodium alginate solution. 100 ml of 2% sodium alginate solution, containing no active agent, was processed concurrently with these 'composite gels' to serve as a control. The solutions were mixed well, centrifuged at low speed to remove air bubbles, and then overlayed with 0.2 M  $\text{CaCl}_2$  solution to form the calcium alginate composite and control

gels. The gels were allowed to set fully for about 48 hr. and then sliced into cubes. The cubes were then soaked in distilled water to remove excess  $\text{CaCl}_2$  and soluble fractions of the humic and tannic acids. These 5 gels were then subjected to the solvent exchange and crosslinking procedure as described in EXAMPLE 1. The dried, crosslinked materials were ground using a Wiley bench mill and passed through a stainless steel 40 mesh screen before use in the copper binding experiment 10 described below.

The ability of the control and composite crosslinked materials to remove copper ions from aqueous solution was determined according to the following protocol: Duplicate samples of 40 - 50 mg of 15 each material were prewetted and washed as described in EXAMPLE 12. A stock solution of  $\text{CuSO}_4$ , containing 1000 ppm Cu, was prepared and diluted appropriately with distilled water to yield standard solutions at nominal concentrations of 25, 50, 100 and 250 ppm of Cu. The 20 pH's were adjusted to 5.5, and the exact concentrations were determined by atomic absorption spectroscopy (AAS). Duplicate 100 ml aliquots of each solution were added to erlenmeyer flasks containing prewet, washed sorbent. The flasks were then incubated with shaking 25 for 2 hrs at 30 C. Following this contact period, the supernatants were analyzed for copper content by AAS, and the amount of copper uptake was calculated by difference. Blank vessels were also processed to verify that no background binding occurred.

30 Results of this copper binding experiment are presented in the tables below. The figures shown are the mean values from two observations at each exposure level. As can be seen in the data below, the inclusion of either humic acid or tannic acid within the 35 crosslinked alginate matrix significantly enhanced the

observed capacity for copper binding compared to the crosslinked matrix containing no active agent.

COPPER UPTAKE CAPACITY BY CROSSLINKED ALGINATE  
5 CONTROL MATRIX AND HUMIC ACID AND TANNIC  
ACID COMPOSITES

CROSSLINKED ALGINATE CONTROL MATRIX

10	INITIAL EXPOSURE	SOLUTION EQUILIBRIUM		CAPACITY	
		LEVEL (PPM)	CONCENTRATION (PPM)		
21.4		5.6		1.58	31.5
		42	22	2.0	39.8
15	98	69		2.9	57.1
		250	220	3.0	59.6

CROSSLINKED HUMIC ACID + ALGINATE MATRIX

20	INITIAL EXPOSURE	SOLUTION EQUILIBRIUM		CAPACITY	
		LEVEL (PPM)	CONCENTRATION (PPM)		
22.6		0.6		2.2	54.3
		50	21.1	2.89	71.7
25	101	70.9		3.01	75.3
		250	211.5	3.85	96.5

CROSSLINKED TANNIC ACID + ALGINATE MATRIX

30	INITIAL EXPOSURE	SOLUTION EQUILIBRIUM		CAPACITY	
		LEVEL (PPM)	CONCENTRATION (PPM)		
22.6		0.4		2.22	48.9
		50	14.4	3.56	79.1
35	100	65		3.60	80
		250	205.6	4.5	98.9

EXAMPLE 16

## PREPARATION OF CROSSLINKED GELATIN MATRIX

5        Five grams of gelatin (275 bloom\*) were mixed with  
100 ml of distilled water and heated to 90 - 100 °C  
with stirring. Upon complete dissolution of the  
granular gelatin, the solution was allowed to cool to  
room temperature, thus gelling the proteinaceous  
10 material. The gel was then sliced into cubes of  
approximately 1 cc volume, transferred to a 250 ml  
round-bottom flask and then subjected to the solvent  
exchange and crosslinking procedure as described in  
EXAMPLE 1. The crosslinked product was then washed  
15 with fresh toluene, dried in a vacuum oven, and ground  
to a powder (less than 40 mesh). The table below lists  
the physical properties of the final material.

\* -See Mantell Thomas C.L., Water-Soluble Gums,  
Reinhold Publishing Co. (New York), 1947, pp. 174 and

20      209.

PROPERTIES OF CROSSLINKED GELATIN

Apparent Bulk Density	0.119 g/cc
Surface Area	110 m <sup>2</sup> /g
Pore Volume	1.31 cc/g
25      Pore Area	151 m <sup>2</sup> /g
Average Pore Diameter	350 Angstroms

WHAT IS CLAIMED IS

1. A porous body derived from a polymeric material other than chitosan, said body having an open-celled 3-dimensional lattice structure, a density of less than 5 1.0 g/cc and a surface area equal to or greater than 85 m<sup>2</sup>/g.
2. A porous body derived from chitosan, said body having an open-celled 3-dimensional lattice structure, a density of less than 1.0 g/cc and a surface area 10 equal to or greater than 200 m<sup>2</sup>/g.
3. The porous body of claim 1, wherein the body is derived from a polymeric gel-forming material.
4. The porous body of claim 1 or 2, wherein said body has a pore volume of at least 0.5 cc/g.
- 15 5. The porous body of claim 1 or 2, wherein said body has an average pore diameter of at least 50 Angstroms.
6. The porous body of claim 1 or 2, wherein said body has less than 50% yield at 200 psi.
- 20 7. The porous body of claim 1, wherein said body has a surface area of at least about 200 m<sup>2</sup>/g.
8. The porous body of claim 1, wherein said body is derived a naturally occurring or synthetic polysaccharide.
- 25 9. An apparatus comprising (1) a vessel which comprises an inlet and outlet means for inflow and outflow of the fluid stream and (2) the porous body of claims 1 and 2.
10. A method for the removal of one or more 30 desired material from a fluid stream containing the desired material comprising contacting fluid stream with one or more porous bodies of claims 1 and 2.
11. The method of claim 10, wherein said desired material is a metal.
- 35 12. The method of claim 10, wherein said desired

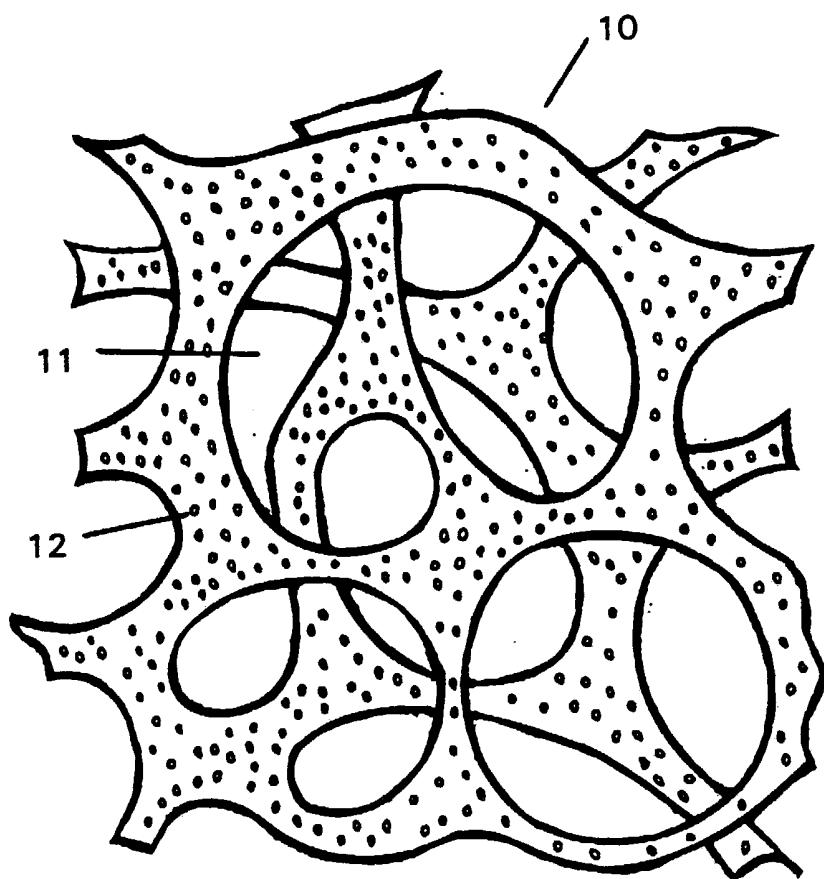
material is an inorganic or organic pollutant.

13. A composition comprising an active agent and at least one porous body of claims 1 and 2.

14. A process for preparing a porous bodies, which  
5 has an open-celled 3-dimensional lattice structure, a density of less than 1.0 g/cc and a surface area equal to or greater than 85 m<sup>2</sup>/g, comprising:

- (a) forming a gel of a desired configuration;
- (b) (i) preparing the gel for crosslinking by  
10 replacing the initial gelling solvent directly or indirectly with a crosslinking solvent which does not react with a crosslinking agent by employing a concentration gradient of solvent to replace  
15 the gelling solvent;
- (ii) adding an effective amount of crosslinking agent; and
- (c) separating the crosslinked body from the crosslinking solvent.

1 / 1 2

**Figure 1**

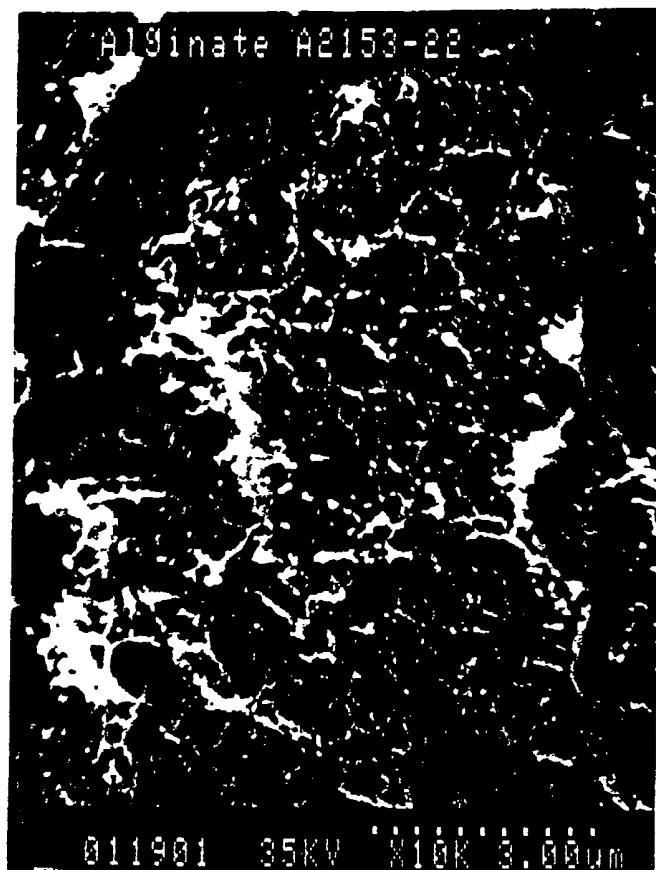
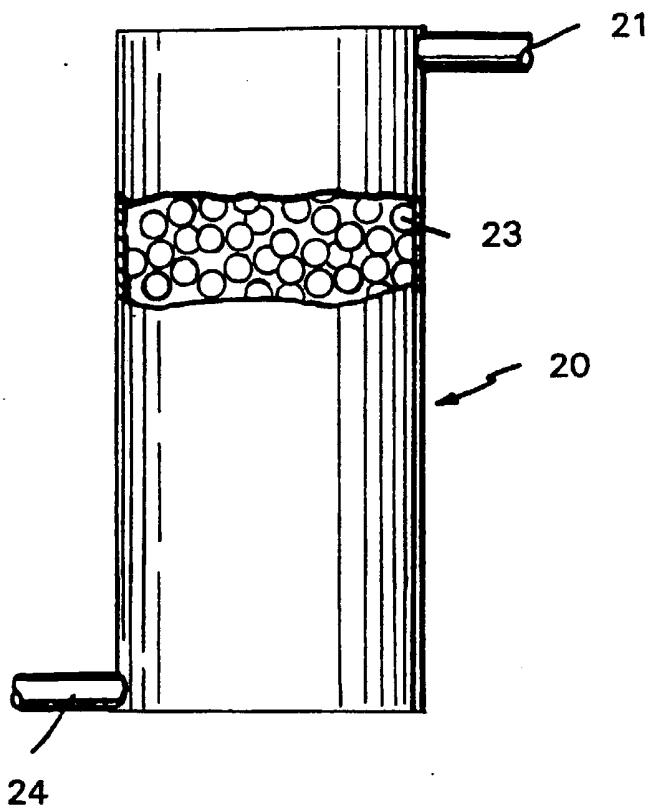


Figure 2

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**Figure 3**

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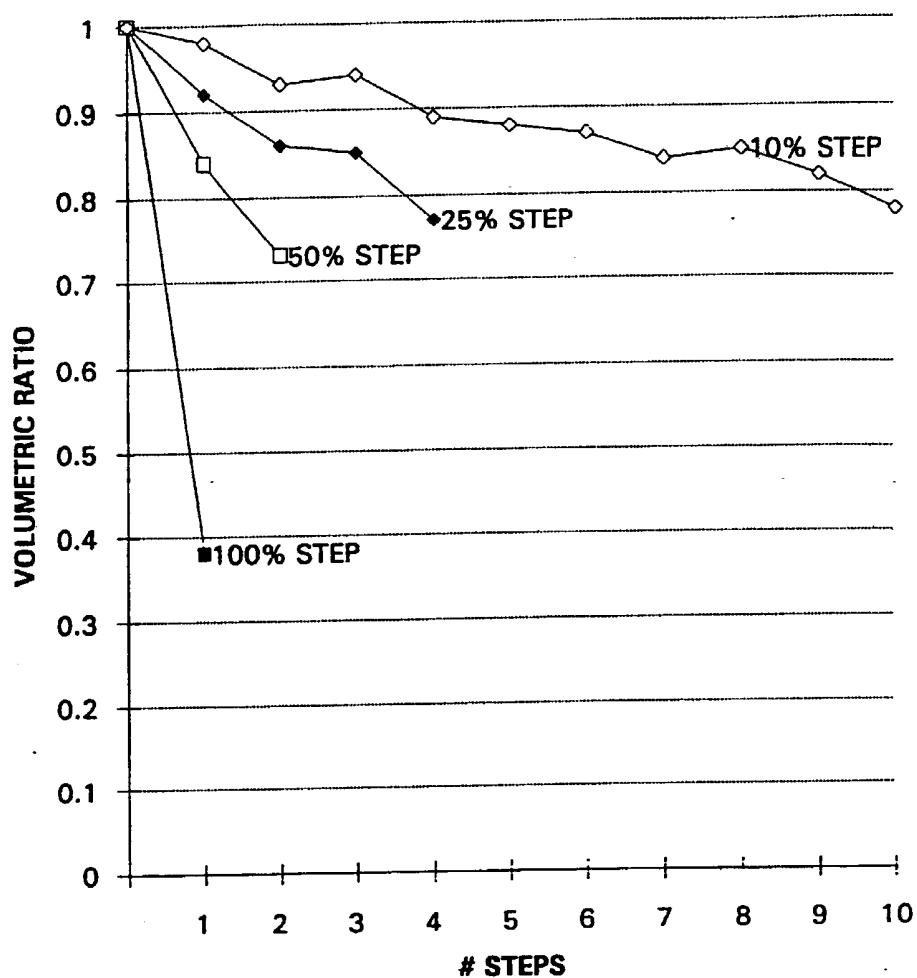


Figure 4

5 / 12

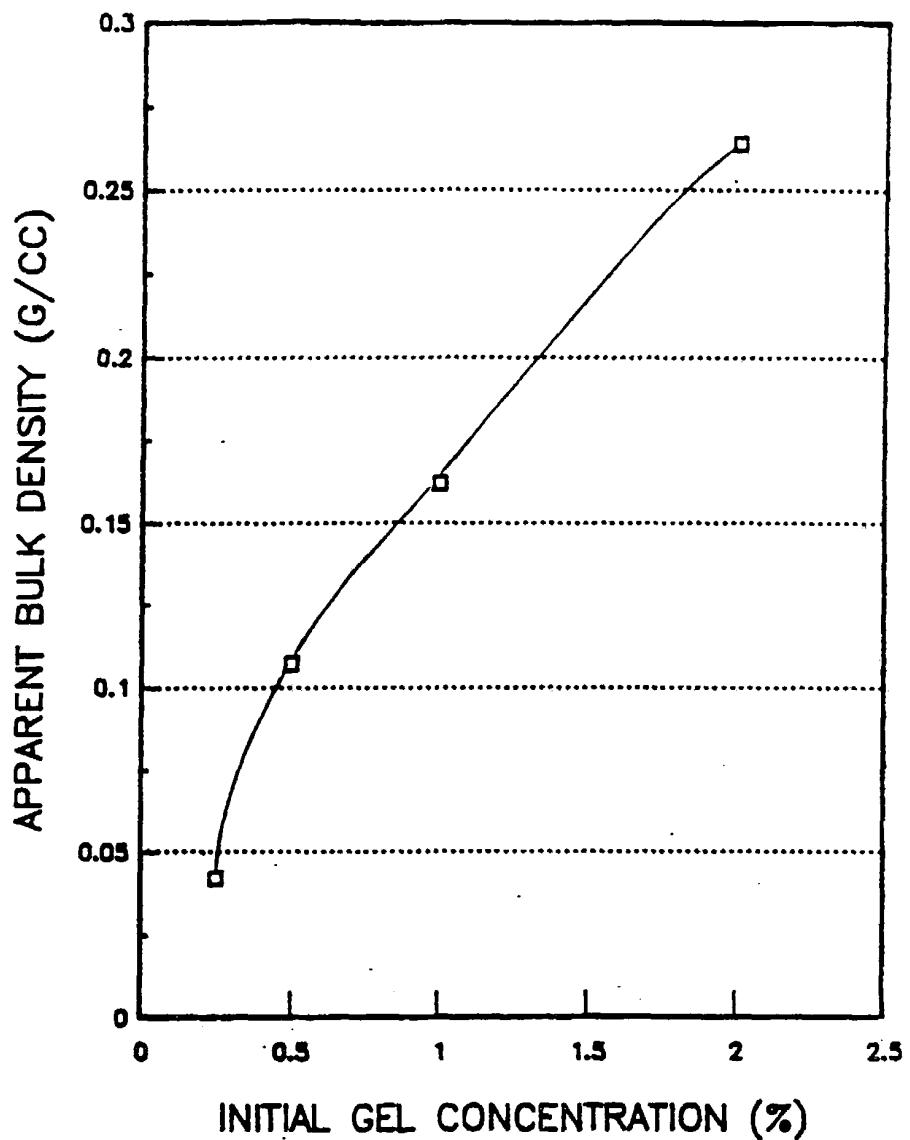


Figure 5

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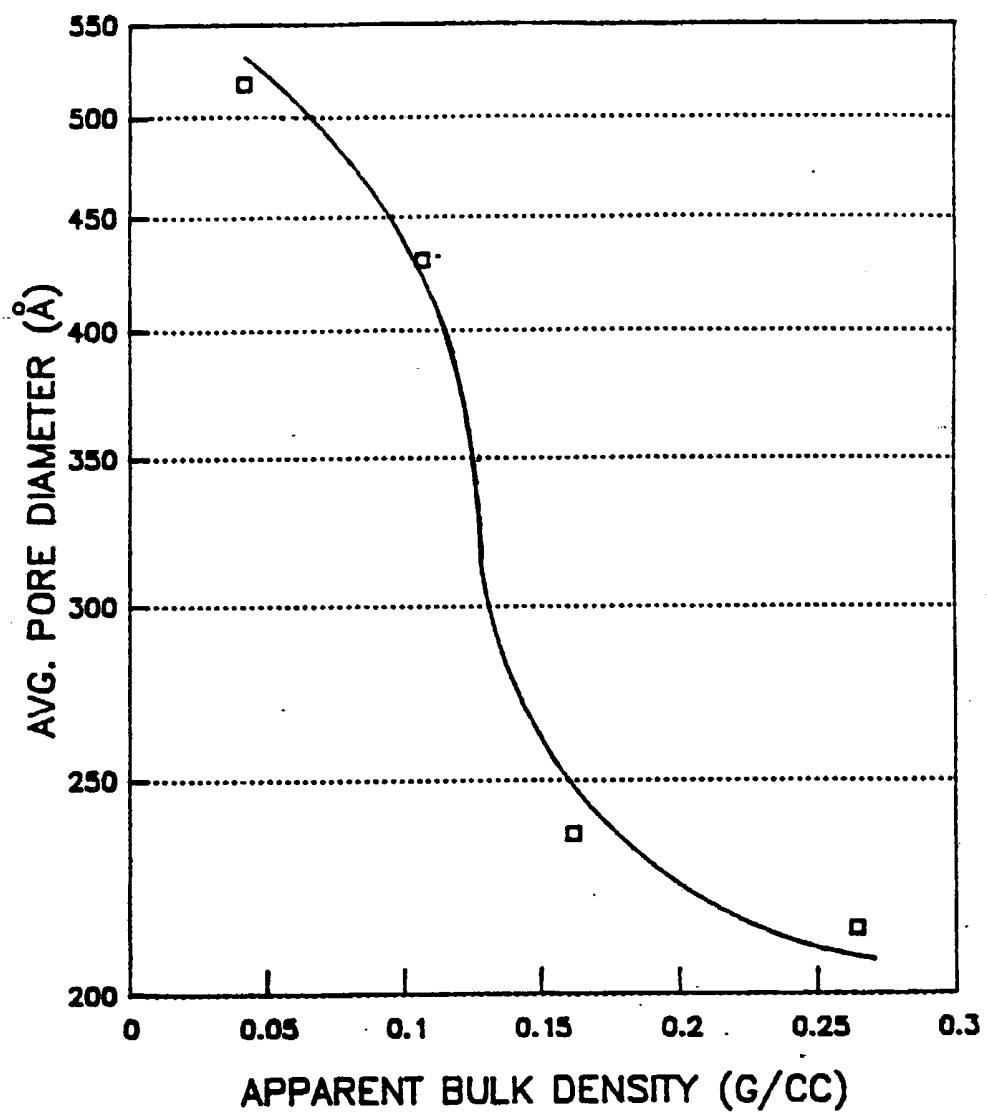


Figure 6

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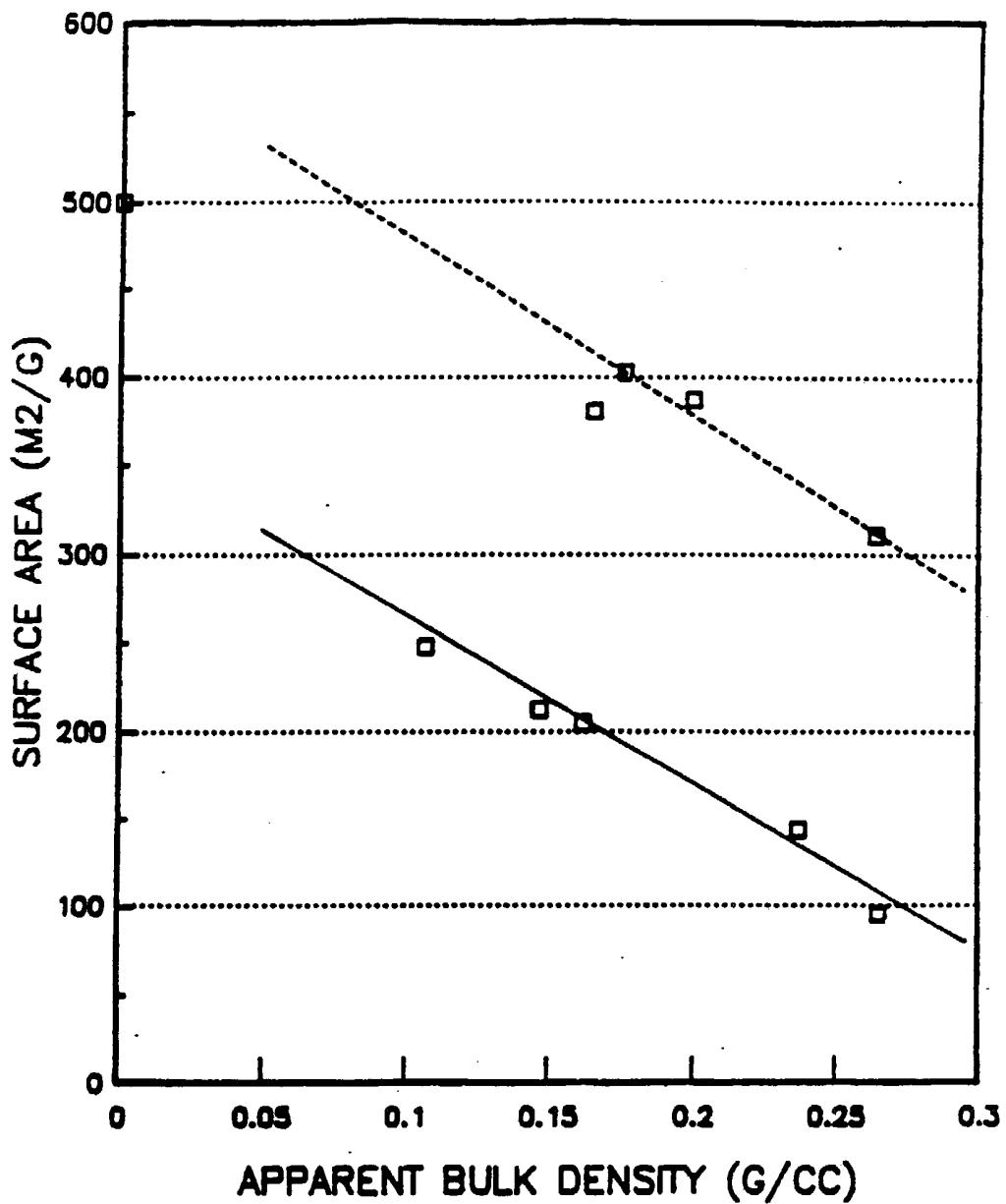


Figure 7

8 / 1 2

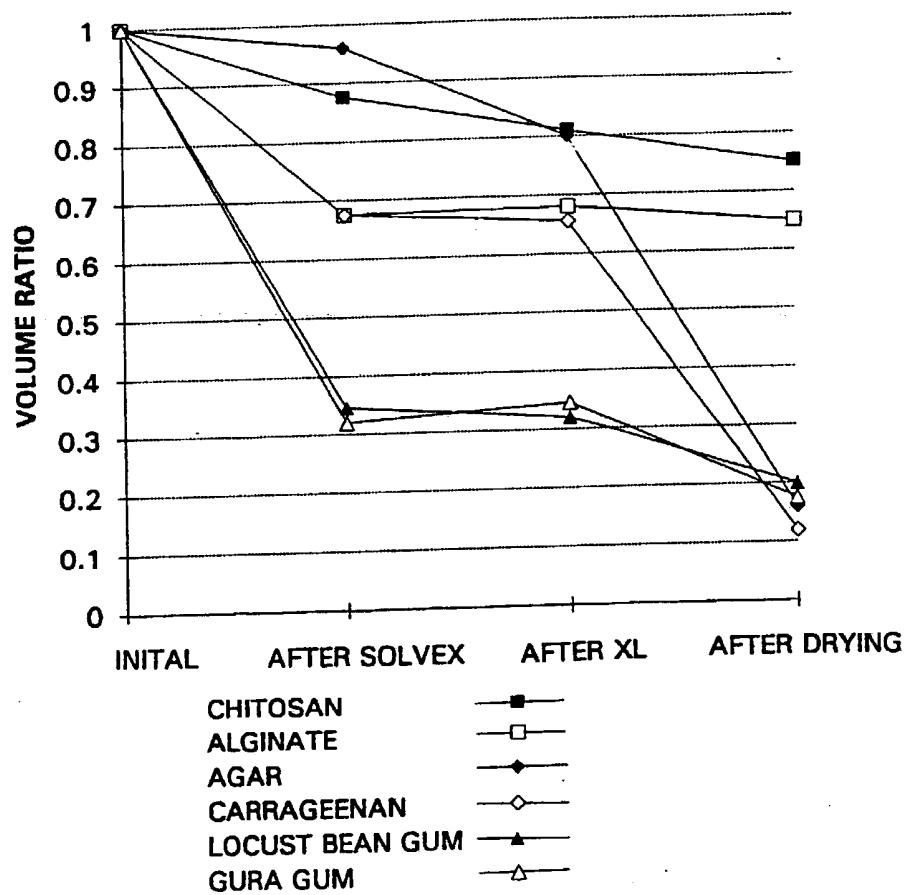


Figure 8

9 / 1 2

10 PPM EACH METAL

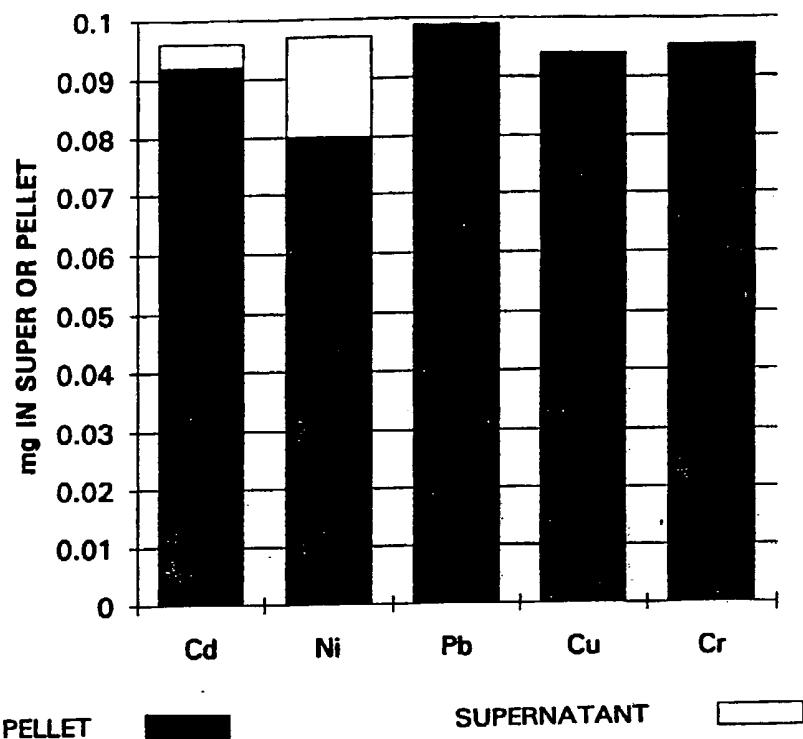


Figure 9(a)

10 / 12

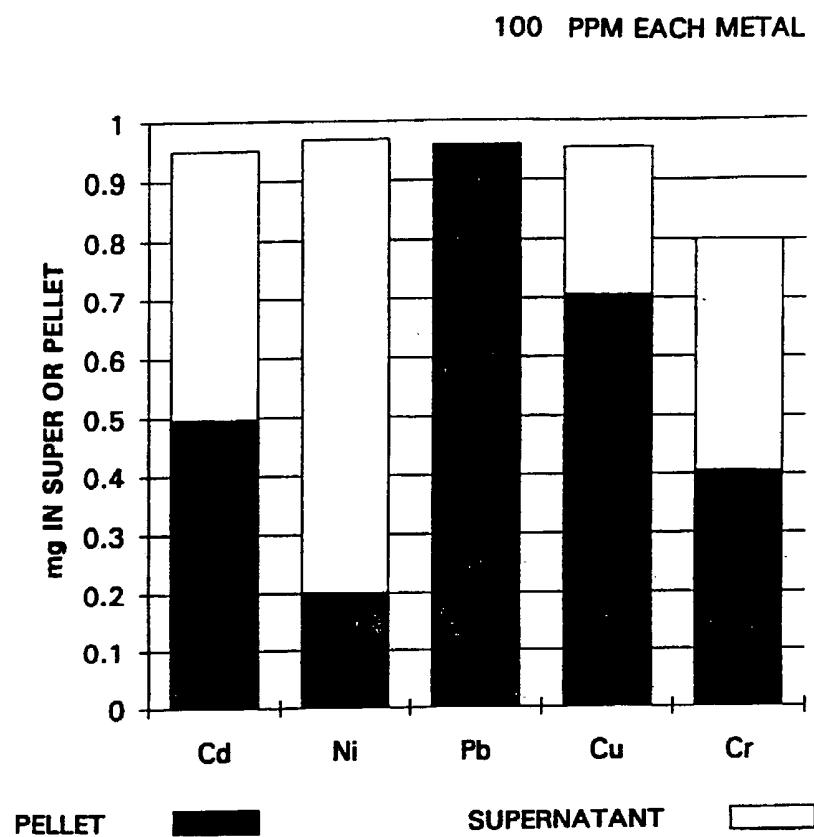


Figure 9(b)

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1000 PPM EACH METAL

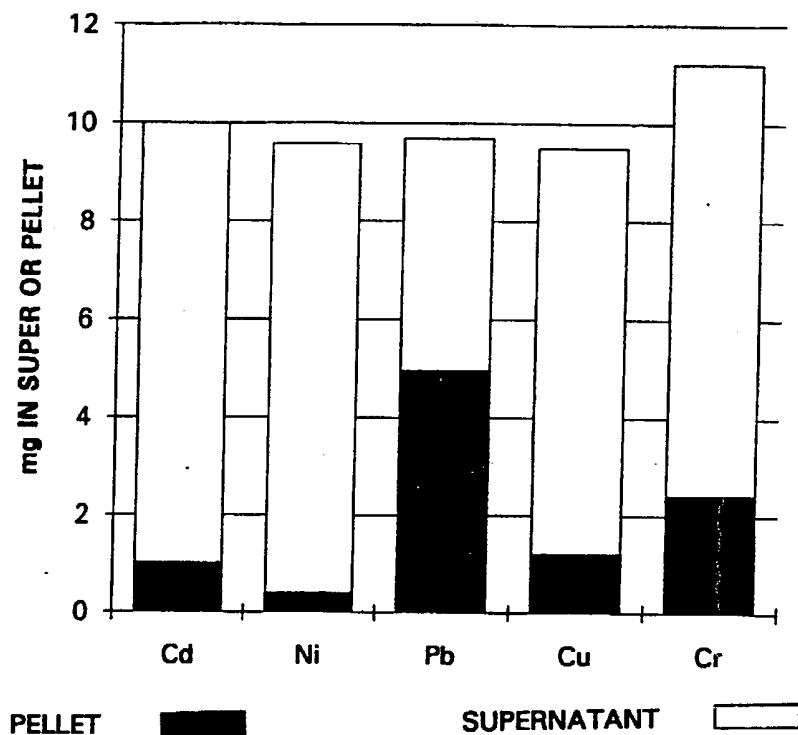


Figure 9(c)

12 / 12

10 PPM EACH METAL

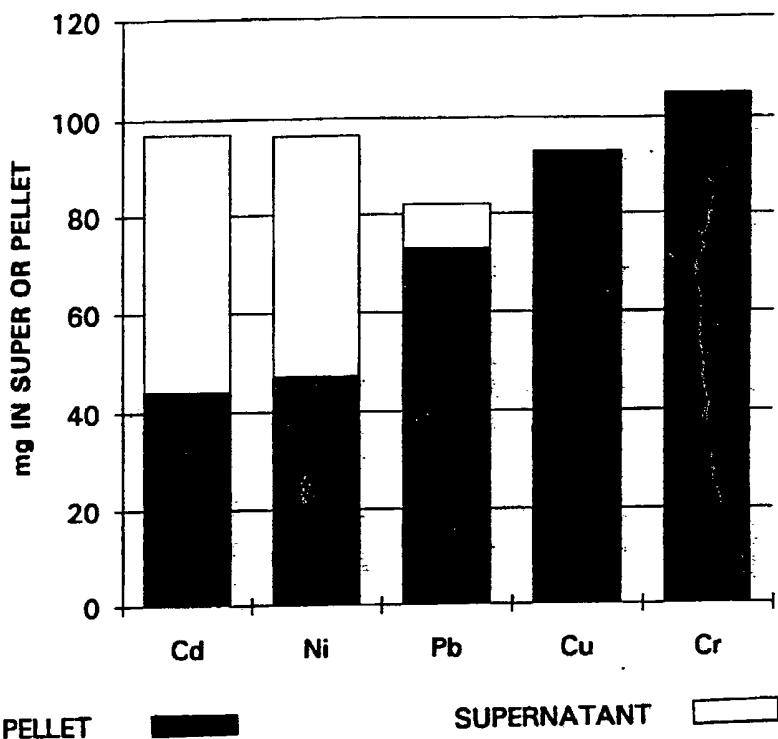


Figure 10

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/10567

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 B01J20/24; B01J20/26

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System	Classification Symbols
Int.C1. 5	B01J ; C08J

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	US,A,4 966 919 (WILLIAMS) 30 October 1990 see column 3, line 65 - column 6, line 51 see column 8; example 2 ---	1
A	KUNSTSTOFFE vol. 71, no. 3, March 1981, pages 183 - 184 KLAUS SCHNEIDER 'MIKROPORÖSE POLYMERE' see page 184, column 1, paragraph 1 ---	5,6,13
Y	FR,A,2 282 905 (INTERN. PAPER CO.) 26 March 1976 see page 29 - page 30; claims 1-16 ---	1
A	EP,A,0 289 238 (UNILEVER) 2 November 1988 see page 3, line 3 - page 5, line 20 ---	1,5,8
A		1,3,4,5, 10,12
		-/-

<sup>10</sup> Special categories of cited documents :<sup>10</sup><sup>"A"</sup> document defining the general state of the art which is not considered to be of particular relevance<sup>"E"</sup> earlier document but published on or after the international filing date<sup>"L"</sup> document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<sup>"O"</sup> document referring to an oral disclosure, use, exhibition or other means<sup>"P"</sup> document published prior to the international filing date but later than the priority date claimed<sup>"T"</sup> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<sup>"X"</sup> document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<sup>"Y"</sup> document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<sup>"&"</sup> document member of the same patent family

## IV. CERTIFICATION

1.

Date of the Actual Completion of the International Search

19 MARCH 1993

Date of Mailing of this International Search Report

17 04. 93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

WENDLING J.P.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	GB,A,2 178 447 (YEDA RESEARCH AND DEV. CO.) 11 February 1987 see page 7; claim 1 ----	1
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A	DATABASE WPIL Week 8631, Derwent Publications Ltd., London, GB; AN 86-200938 & JP,A,61 133 143 (FUJI SPINNING) 20 June 1986 cited in the application see abstract ----	9,10,12, 13
A	DE,A,3 527 482 (FUJI SPINNING) 6 February 1986 see page 17 - page 21; example 1 see page 41 ----	11
A		2
A		9

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9210567  
SA 68055

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 19/03/93

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